United States Court of Appeals

for the

District of Columbia Circuit

TRANSCRIPT OF RECORD

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OCTOBER TERM, 1940.

No. 7791

725

THE DOW CHEMICAL COMPANY, APPELLANT,

vs.

CONWAY P. COE, COMMISSIONER OF PATENTS.

APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF COLUMBIA.

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United States Court of Appeals for the District of Columbia

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a. District Court of the United States
For the District of Columbia

Civil Action No. 2924

THE DOW CHEMICAL COMPANY, *Plaintiff,*

v.

CONWAY P. COE, Commissioner of Patents, *Defendant.*

UNITED STATES OF AMERICA,
District of Columbia, ss:

BE IT REMEMBERED, that in the District Court of the United States for the District of Columbia, at the City of Washington, in said District, at the times hereinafter mentioned, the following papers were filed and proceedings had, in the above-entitled cause, to wit:

1 *Complaint*

Filed May 31 1939

In the United States District Court
For the District of Columbia

Civil Action No. 2924
Action under 4915 RS

THE DOW CHEMICAL COMPANY, Midland, Mich., *Plaintiff,*

v.

CONWAY P. COE, Commissioner of Patents, *Defendant.*

Plaintiff states as follows:

1. The plaintiff, The Dow Chemical Company, is a Michigan corporation having its principal office and place of business at Midland, County of Midland, State of Michigan and brings this suit in its own right.

2. The defendant, Conway P. Coe, is the Commissioner of Patents of the United States, an official resident of the Dis-

trict of Columbia, and is sued as Commissioner of Patents of the United States.

3. This bill is filed in accordance with the provisions of Section 4915 of the Revised Statutes of the United States.

4. The plaintiff is by direct assignment the owner of the entire right, title, and interest in and to the application of Edgar C. Britton, Carl F. Prutton, and Jack L. Williams for a patent in the United States Patent Office entitled "Production of Alkyl Halides" which was filed on 1935 October 9 and given Serial Number 44 252.

5. The said application was filed in accordance with the laws of the United States and the rules of the Patent Office.

2 6. The said application has been duly prosecuted in accordance with the laws of the United States and the rules of the Patent Office.

7. Said application has been passed upon by a Primary Examiner of the Patent Office who refused to allow claims 22 to 34, inclusive:

22. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

23. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chloroethane derivative having a boiling point higher than that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

24. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chloro-ethylene derivative having a boiling point above 40° C., while the bath is maintained at a temperature

between 12° and 40° C. and under approximately atmospheric pressure.

25. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachlorethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

26. In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

27. In a process for the production of ethyl chloride, the
step which consists in passing, in substantially equi-
3 molecular proportions, ethylene and hydrogen chlor-
ide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachlorethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

28. In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethylene and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

29. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anyhdrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydro-

carbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

30. In a process for the production of ethyl chloride, the steps which consist in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

31. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the step which consists in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

32. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under 4 substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

33. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

34. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

Said claims 22 to 34, inclusive, were, by the Primary Examiner, twice and finally rejected.

8. The said applicants appealed from the decision of the Primary Examiner to the Board of Appeals, who affirmed the rejection by the Primary Examiner in their decision dated 1939 April 7, all of which appears from the file of the application, profert of which is hereby made.

9. The Commissioner of Patents, by the Primary Examiner and the Board of Appeals, has held that the said claims are unpatentable because anticipated by the disclosure of the patent to Curme, 1 518 182, and the patent to Nutting et al, 2 007 144.

10. The plaintiff charges that this ruling of the Commissioner of Patents is erroneous and that claims 22 to 34 are patentable.

11. The plaintiff further states that the invention defined by said claims is new and useful and was not known

or used by others in this country before the invention thereof by Britton, Prutton, and Williams, and not patented or described in any printed publication in this or any foreign country before the invention thereof by Britton, Prutton, and Williams, or more than two years prior to the filing of said application for patent therefor, and not in public use or on sale in this country for more than two years prior to said application, and not patented in any foreign country by plaintiff, the inventors, or the legal representatives of either on an application filed more than twelve months prior to said application for United States patent, and has not been abandoned.

Wherefore the plaintiff prays that the Honorable Court decree that the Commissioner of Patents be directed to allow the said claims.

THE DOW CHEMICAL COMPANY (Seal)
By WILLARD H DOW,
President

NELSON J JEWETT
Plaintiff Solicitor

RUSSELL WILES
Of Counsel

STATE OF MICHIGAN
County of Midland, ss.

I, Willard H. Dow, depose and say that I am the President of The Dow Chemical Company; that I have read the above bill by me subscribed and know the contents thereof; that the statements of fact therein made as upon personal knowledge are true and those made upon information and
belief I believe to be true; and that I am authorized
6 to sign this bill by the Board of Directors of said The
Dow Chemical Company.

WILLARD H DOW.

Sworn to and subscribed before me this 25 day of May, 1939.

LEW A. CHICHESTER
(Notarial Seal) *Notary Public*

My Commission Expires April 13, 1941

7 *Answer to the Complaint.*

Filed June 24 1939

* * *

To the Honorable the Justices of the District Court of the United States for the District of Columbia.

1. Defendant admits the allegations of the incorporation and principal place of business of the plaintiff.

2. He admits the allegations of his official position and official residence.

3. He admits the allegation of jurisdiction.

4. He admits that plaintiff is the owner of the application of Edgar C. Britton, Jack L. Williams and Carr F. Prutton, for a patent on improvements in Production of Alkyl Halides, which application was filed on October 9, 1935, and given Serial No. 44,252.

5. He admits, for the purpose of this suit, that the application was duly filed.

6. He admits that it was duly prosecuted.

7. He admits that the primary examiner finally rejected claims 22 to 34, inclusive, set out in paragraph 7.

8. He admits that on appeal the action of the examiner was affirmed by the Board of Appeals.

9. He admits the allegation of paragraph 9.

10. He denies that the refusal to issue to plaintiff a patent containing said claims was erroneous and denies that said claims are patentable since they are deemed to be unpatentable over the following prior art and for the reasons given in the statement of the examiner in answer to the appeal and the decision of the Board of Appeals, copies of which will be presented at the trial:

Curme,	1,518,182,	Dec. 9, 1924,
Nutting et al.,	2,007,144,	July 2, 1935.

8 Profert of copies of these patents is hereby made.

11. He admits that in the oath to said application the applicants Edgar C. Britton, Jack L. Williams and Carl F. Prutton made averments corresponding to the allega-

tions of paragraph 11, but denies that these allegations are sufficient to justify the issuance to plaintiff of a patent containing the said claims.

R. F. WHITEHEAD
Solicitor for the Patent Office,
Attorney for Defendant.

June 23, 1939.

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9 *Transcript of Proceedings*

Filed October 28 1940

* * *

Proceedings had before the Honorable Justice J. Bailey, one of the Judges of said Court, commencing June 13, 1940, at 10:45 o'clock A. M.

Appearances:

Chritton, Wiles, Davies, Hirschel and Dawson By Russell Wiles, Esq.,

The Commissioner of Patents, By Joseph L. Kelly, Esq., William Takacs, Esq.

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Mr. Wiles: This case, of course, is here in the usual way. It is admitted there was proper prosecution in the Patent Office, no informalities about it. It was regularly rejected by the Primary Examiner and confirmed by the Board. It involves a chemical process for the manufacture of ethyl chloride out of ethylene gas and hydrochloric acid gas. The ordinary hydrochloric acid is a solution in water; this is a dry hydrochloric acid.

To illustrate (and I see your Honor has considered a chemical case, as illustrated on the blackboard)—

The Court: I didn't learn much, however.

Mr. Wiles (continuing): To illustrate what these gases are I use this illustration (indicating). The yellow represents hydrogen and the green represents chlorine. Now, as your Honor may have learned in other like cases, the
11 carbon atoms are supposed to have four bonds or union points; when they are thoroughly saturated they will take four hydrogens and they may be connected up in rings, chains, all sorts of conglomerations such as are illustrated upon the blackboard in the case you heard recently.

Ethylene is one of the so-called unsaturated hydrocarbons. In that, two of the carbon atoms are connected together by two bonds instead of one, and that is also termed unsaturated. Those could be disconnected and an extra hydrogen put on each end; then we would have what we call a saturated hydrocarbon. The unsaturated has the double bond between carbons (illustrating). Ethylene is obtained mostly these days as a by-product of petroleum oil, available in considerable quantities. Ethyl chloride is used extensively as a reagent and for other purposes, and we want to make it by hitching on, taking a hydrochloric acid, which would be this one (illustrating), one hydrogen against the one chlorine, and break these double bonds apart and put the hydrogen from the hydrochloric acid on one end and the chlorine on the other. So you pull them apart this way (illustrating). The hydrogen of the hydrochloric acid goes on in the manner I have illustrated and then the chlorine goes on there (indicating). And then you have what is called ethyl chloride. That is a saturated hydrocarbon— the chlorine has taken the place of one hy-

drogen and the reaction has taken place on the so-
12 called double bond of the original ethylene.

Now the position of the Board, I should say, at one time this case was practically allowed by the Primary Examiner. He must have been very gravely in doubt about the matter because he had the references before him and held these claims were patentable, for a long time. Something then occurred to change his mind. We can't find fault about that, of course, because if he made an error obviously he should have corrected it. Nevertheless it is close enough, a year or two, the Examiner thought this was a patentable thing.

Of course this reaction I have described where we take ethylene and add a hydrochloric acid on the double bond, one of the hydrogens going to one carbon, the other to the other, is not a new reaction. We are not claiming that broadly at all; we are claiming a continuous process which accomplishes the result very rapidly, very inexpensively, very easily, and with an extremely high yield.

In a broad way, what is done is to have a solvent bath of, usually, tetrachloroethane. The bath does not make much difference. It is a relatively high boiling bath. For the purpose of the Court's understanding, only certain baths would work and we describe the ones that will work. Its composition isn't very material, I don't think, to you. We use a
liquid bath of fairly high boiling material. We put
13 into it aluminum chloride, which is a catalyst and pro-
duces this reaction very rapidly, and at a low temperature, and we simply feed into this bath ethylene gas-hydrochloric acid gas. They unite under the liquid surface to form ethyl chloride. That is fairly volatile and it boils off just as fast as it is formed. The bath has had considerable of the product in it but it reaches a certain point of saturation, and then the ethyl chloride boils off just as fast as it is formed, is condensed in a condenser, purified, and what not. The process is a continuous one and as a practical matter it has to be carried on at a temperature above the boiling point of ethyl chloride, which is 12° C. and below the boiling point of the bath so the whole bath does not boil off. There is a temperature range in that that is all specified in the claims at which this thing has to be carried on to work properly. The process is extremely useful.

I should say these temperatures are very ordinary temperatures. I mean they are not high temperatures requiring a great deal of heat. This will run, I think, at ordinary room temperature, or a little higher. The ethyl chloride, which is quite volatile, boils off, and the thing proceeds and they get an actually effective yield of 90% to 95% of the total ethylene and hydrochloric acid that is put in out in the form of the ethyl chloride they want. The process runs
14 for weeks and months at a time; it is a perfectly smooth operation. They have to add aluminum chloride from time to time; some of the bath is carried away and they add to that. So the process is caried on from week to week, one of the simplest and most beautiful processes I have ever run into.

Now, the Patent Office has rejected this principally on a patent to Nutting, et al., taken together with a patent to Curme. Curme discloses this basic reaction but not a continuous process at all. The conditions are simply different but this basic reaction of adding hydrochloric acid to ethylene is disclosed by Curme. The major reference the Patent Office has relied upon is a patent to Nutting et al. owned by the plaintiff here.

Now, the Nutting patent has nothing to do with making this kind of a product or this process. Nutting has a process that is chemically somewhat analogous. I mean, to look at it superficially, one would say it is suggestive of Nutting. Nutting starts with what is called vinyl chloride. That is an unsaturated hydrocarbon with a double bond but it already has one hydrogen substituted by chlorine—that is vinyl chlorine. He wants to add hydrochloric acid at the double bond to make what is called ethylidene chloride, and he does it with aluminum chloride as a reagent and he gets this product that I am showing you now (illustrating). You will see that has two chlorines on it as distinguished from this one (illustrating) which has but one.

15 The Patent Office, the Board particularly, proceeded on the theory that vinyl chloride and ethyl chloride are so closely analogous that anything one would do, the other would; that they are much alike, both of them double-bond, differing only in that one has the chlorine where there was hydrogen on the other; that you could just reason by analogy one to the other.

This Nutting patent, in the main, is not on any continuous process at all; it is on a batch process where you take a certain amount of vinyl chloride, a certain amount of hydrochloric acid, mix them, and produce the reaction. But you don't distill off the product as it is formed. It isn't continuous in any sense whatever. Nutting says on Page 2 (and this is the thing the Patent Office was interested in) . . . "A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed. Any hydrogen chloride and vinyl chloride which pass through the mixture without reacting may readily be separated from the product and recycled in the process. By operating in such manner, the process is made continuous and the quantity of catalyst required to produce a given quantity of ethylidene chloride is reduced materially."

16 That is a clear and a definite suggestion of a continuous process and very much like the one we are dealing with. The Patent Office simply took the position here is this continuous process outlined where you are using vinyl chloride, substituting instead of vinyl chloride ethyl chloride, and to have the same kind of reaction take place would not be inventive—anybody ought to be able to look at one and see the other would take place.

The case was prosecuted through the Patent Office on the evident theory that the Patent Office was wrong in its law on that subject because, generally speaking, the courts have held by a vast majority that in chemistry the results are so unpredictable that you cannot rely on reasoning by analogy from one process to another. I think the great weight of authority is that way.

When it became necessary to bring this suit I was consulted. I wasn't in the prosecution at all. We then caused this statement that I have just read your Honor in the Nutting patent to be thoroughly investigated. It was all in our own Dow plant but the two men are in different departments, and the work never got together. We discovered not only had that statement not been adequately investigated but it is just untrue that that whole scheme outlined in this Nutting excerpt I read, beginning on line 4 of page 2 and

running down to line 17, which is the part the Patent Office relied on, just won't work. Therefore, there has been
17 filed in the Patent Office a disclaimer of that part of
the Nutting patent which the Office has particularly stressed, and the claims based upon it have been disclaimed out of the patent. That will be part of my evidence.

Now, this discovery that these things don't work because the ethyl chloride process does work beautifully, emphasizes the soundness of those courts which said . . . "we won't reason by analogy in these chemical reactions". What actually occurs, as we will show you, when we take the mixture that Nutting and his colleagues suggest, the reaction takes place to a certain extent but to a much greater extent the polymerization of vinyl chloride takes place.

Now, vinyl chloride is a product which polymerizes with very great ease to make heavy, tarry, gummy masses. In fact, that type of product is used a good deal in plastic work of one sort of another, because it does. This product, subjected to the action of aluminum chloride, which is a violent catalyst, simply goes to gummy material that within a very few hours stops the entire process completely. I mean the apparatus just plugs up with a gummy, tarry material, and won't work at all.

In addition, the end product that Nutting was trying to make, ethylidene chloride, decomposes with great ease and goes back to what it was, and then the vinyl chloride tries to recombine, polymerize, so that the ultimate yield
18 of material is extremely poor. In other words, if you
set up the apparatus and run the Nutting process in it, in the course of perhaps three or four hours this apparatus will become entirely plugged up and no good. It simply cannot go on. You would have made so little it wouldn't have paid you to run the process at all, because the cleaning out of the apparatus would have made the product you got hopelessly useless, and you would have made into product only about 30% of the vinyl chloride you put in, whereas the process started with ethylene runs weeks and months with no difficulty, no gumminess, giving a yield of 90 to 95%. Had we only shown how to increase the yield from 30 to 40% to over 90%, we would have had a patentable thing if changing the reaction of one thing to another would have produced that alteration.

But we have gone much further and shown that part of the reference is utterly misleading and essentially incorrect, really an inoperative part. The moment the investigation was made for the purpose of this suit, we concluded that it would be necessary to draw a disclaimer up and take that part out of the Nutting patent because it is so misleading. I have no doubt had those facts been before the Office the case would have been allowed. I think with that reference in their possession (as our factual evidence will show) the
thing wouldn't have been insisted upon at all by the
19 Office. It is not only demonstrates that the Nutting
reference is ineffective, is inoperative and a misleading reference, but, as I say, it beautifully demonstrates the general rule the courts have laid down you ought not to rely on analogies between these processes.

The fact is while ethylene and vinyl chloride are very much alike structurally, the only difference being there would be a hydrogen where I had a chlorine on this raw material form, you glance at them and say maybe they ought to do about the same thing. The chemical fact is that ethylene, when you take this chlorine off and put a hydrogen on in place of it, is relatively stable; carrying out reactions with it is relatively different, requiring generally higher temperatures and all that sort of thing; whereas the vinyl chloride is so highly reactive it reacts with itself to make these tars.

It is a fact that you cannot reason in this particular case from one to the other at all, and we will demonstrate that by the testimony of chemical experts. I think that is the factual matter that I am going to introduce.

As to the legal matters, I presume your Honor is familiar with the line of cases that govern these things.

The Court: I can't say I am familiar with anything in patent law.

Mr. Wiles: I hope I am not going to say some-
20 thing that is irrelevant. The courts of the United
States in the trial of patent cases have been extremely rigid in not reasoning by analogy from one thing to another. I took . . . well, a defeat that hurt me plenty in the Sixth Circuit when Judge Dennison was here. A bath with a little bit of nitric acid in it; they precipitated lead sulphate by pouring in sulphuric acid; another man came along and

precipitated by pouring in lead arsenate from the same arsenic bath. The court held the patent was perfectly good because of not reasoning by analogy in chemical cases.

I remember having the same situation arise in the Eighth Circuit. My adversary was arguing and one of the judges leaned over (I have forgotten which one) and said: "Don't you think if we try to rely on chemical analogy we are trying to rely on something very frail?"

Now, the courts that try patent cases practically refused to reason from one chemical compound to another at all. The Patent Office I think, generally speaking, does follow the courts, but there are a good many Examiners, and I think some members of the bar, who just positively refuse to follow the court rule. They say the courts have gone too far and they don't recognize enough chemical skill. Now, if we take the decisions of the trial courts as they are, there wouldn't be any need for our being here at all. The Supreme Court of the United States in the last chemical
21 case they had, I believe, speaking by Mr. Chief Justice
Taft, held it was reasonable to shift from one member to the next of one of these analogous series. The art was triphenyl guanidine used as a rubber accelerator and the Supreme Court held patentable diphenyl guanidine, the next of the series.

Anybody would probably guess if one worked the other ought to. I mean that would be a reasonable guess for a chemist, but it wasn't the kind of thing that the trial courts ever had. The Patent Office has displayed a tendency to be more rigid than the Federal courts on these matters. Even with that, I am very sure that had the factual evidence that we produced been before the Office in this particular case, there is no analogy except the superficial one of the appearance between the vinyl chloride at the start of the art and ethylidene chloride at the finish.

Mr. Kelly: I would like to call this to your Honor's attention—and I might say at the outset, your Honor, I am not a chemist but I have a member of the Bar, Mr. Takacs with me and a member of the Examining Corps who is a chemist, who will assist us—

The Court: You and I start from scratch, then.

Mr. Kelly: Yes, sir. (Continuing) We submit the claims in issue are not patentable over the two references, that is, 1,518,182 Curme, and the patent of Nutting et al., 2,007,144. Without going into the chemistry any more than I feel that we should or have to, I would like to compare the counts, or at least one claim, with the disclosure of these two patents. 22 The plaintiff is asking for some 13 claims on this process. During the appeal they have singled out claim 22 as being representative. The claim calls for—"In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure".

It is to be noted that that claim does not mention continuous process. There are other claims, however, which do claim continuous process.

Now, in the Nutting et al., patent is disclosed a process of making ethylidene chloride which consists in passing vinyl chloride and hydrogen chloride into a liquid reactor bath consisting of aluminum chloride.

I would call to your Honor's attention you have two constituents in common—your reactant, hydrogen chloride, with another material, using aluminum chloride as a catalyst. Furthermore, this catalyst lies suspended in a bath of a chlorinated lower aliphatic hydrocarbon. This patent suggests trichloro-ethane as one such material. This patent suggests a preferred temperature between 15 and 60° C. 23 That is clearly above the 12° C. called for in Claim 22.

As to pressure, the patent states, page 1, column 2, lines 19 to 21—"The reaction may be carried out at atmospheric pressure, but is more rapid and complete at higher pressures".

As to the process being continuous, counsel pointed out in page 2 of the patent the patentee stated it was continuous. I would like to call your Honor's attention to Claim 6 of the Nutting et al., patent which also claims that the process is continuous. Now I am not certain but what that may be one of the claims that counsel for plaintiff has stated that the assignee of this patent has disclaimed, but I don't see that that is of any particular moment here. This patent issued July 2, 1935, and as I understand it, has just been disclaimed. It has been teaching something to the public all these years. I am not certain that an assignee can disclaim something in one patent to make application of claims in another patentable. Whether the claims in the patent are valid or not, they still teach this certain process.

It is to be noted there, I think, the only difference between the disclosure of that patent and the claims in suit is one of the reacting materials that are used. The patent used
vinyl chloride; the plaintiff uses ethylene. Those
24 substances are so closely related, as pointed out to
the Board—and I might say at least one of the members of the Board, Mr. Porter, is a chemical engineer and was Chief Examiner in charge of the Chemical Division for some years before he was appointed to the Board, so I would say that he would be in position to say what a chemist would pick out and what he would not. During the prosecution of the case, the plaintiff objected to the picking out of what they considered desirable features of this patent and then uniting them in the way that the Examiner did to meet these claims. As I have stated, those features were definitely referred by the patentee—not only referred a number of times but he actually claimed some of them.

Now, the other reference, the Curme patent disclosed a method of making the identical substance the plaintiff is making. They use the identical reaction materials—ethylene and hydrogen chloride; they use the identical catalyst—aluminum chloride. They suggest suspending the catalyst in a bath. On Page 1, Line 73 to 76 of the Curme patent is a statement: "The solvent employed"—that is the liquid that would make up the bath—"may be the reaction product, or other suitable solvent, preferably anhydrous."

This Curme patent states the process may be carried out at room temperature. That is clearly above 12° C., this claim by plaintiff.

25 The only real thing lacking or missing in this patent as compared to the claims is that it does not state that the process is continuous and it does not bring out the particular solvent. The Examiner has held, confirmed by the Board of Appeals, that this Curme patent discloses sub-

stantially the process the plaintiff is claiming, and to combine the Nutting patent as to the bath and the continuity of the process would not amount to invention.

Counsel for plaintiff put some stress on the fact that some of these claims have been allowed at one time. I submit, your Honor, that that is of no particular moment here. There are numerous decisions to the effect that the fact a claim is once allowed, there is no reason why it should stand. And, furthermore, if the Examiner was in doubt as to whether or not these patents could be combined the way he combined them to meet the claims, the fact remains that the Board of Appeals not only combined them the way he combined them to meet the claims, but they combined them the other way too. That is, the Board of Appeals said to take the process taught by Nutting et al. and supply the materials taught by Curme, would not be invention. They also said that to take the Curme basic process and to supply the solvent and to carry on the process continuously would not be invention.

I have several decisions that I would call to your Honor's attention later regarding the analogy of chemical
26 patents. There are numerous decisions peculiar to
the fact if one patent suggests the use of a material, even though that particular material in substance is not mentioned, if it is an analogous material, one could be substituted for the other in the same manner as a mechanical patent.

For that reason, your Honor, I submit the claims are not patentable.

Mr. Wiles: One thing I want to make clear to your Honor, I don't believe an owner can destroy a reference by disclaimer. I think it would be terrible law if it could be done. I do say that when the reference is proved to be inoperative by its owner, then he has to disclaim it because it becomes deceptive to the public, as in the case here, and then it isn't a reference and it isn't any better or worse because of the disclaimer. It is the fact that compels the disclaimer that is important, that this statement just isn't true.

(Whereupon at 11:25 o'clock a. m., a short recess was had.)

Henry B. Hass, a witness called herein on behalf of the plaintiff, after first having been duly sworn by the Clerk, testified as follows:

Direct Examination

By Mr. Wiles:

Q. Your full name, please? A. Henry B. Hass—
27 H-a-s-s.

Q. Your occupation? A. I am head of the Department of Chemistry at Purdue University, LaFayette, Indiana.

Q. Will you tell us something about your education and training as a chemist? A. I took my Bachelor's Degree at the Ohio-Wesleyan University, Delaware, Ohio, and went from there to the Ohio State University for my Master's and Doctor's work. Upon leaving the Ohio State University, for three years I was Research Director for the Baltimore Gas Engineering Corporation, after which I became a member of the Faculty at Purdue, in 1928. That was as Assistant Professor. I have been promoted to Associate Professor, full Professor, Director of Research of the Department of Chemistry, and three years ago to head of the Department of Chemistry.

Q. Have you had special experience with the type of chemical compounds that we are dealing with here? A. Yes, sir. I have been awarded the Modern Pioneer Award of the National Association of Manufacturers for research on these chlorine compounds, and also on nitration of similar saturated hydrocarbons.

Q. Have you read the application that is in controversy here and do you understand it?

A. Yes, sir, I do.

Q. And have you read the prior art patents relied
28 on in the Nutting and Curme patents? A. I have.

Q. I wish in your own way you would first describe to the Court what this process here in controversy is, how it operates, and what it does. A. The process in controversy is one consisting of the union of an unsaturated hydrocarbon, ethylene C_2H_4, with hydrogen and chloride, which has the formula HCl. It has always been known that these two substances can combine to form C_2H_5Cl, which is ethyl chloride. That was disclosed by Curme and was known much prior to Curm.

The process in issue consists essentially in four things. These are:

First, the utilization of an aluminum chloride catalyst;

Second, the use of a reaction bath boiling higher than the boiling point of ethyl chloride, the product, and therefore capable of being maintained in the reactor as the ethyl chloride boils away.;

Third, the use of a temperature above the boiling point of ethyl chloride and below the boiling point of the bath; and

Fourth, the use of atmospheric pressure.

These four things conspire to render possible a continuous operation by which the ethylene and hydrogen chloride can be fed continuously into the bath, the ethyl
29 chloride continuously removed by evaporation or
boiling away, and in that way excellent yields of ethyl chloride, a very useful product, are obtained from these cheap reagents—ethylene and hydrogen chloride.

Q. Now, you heard counsel for the Commissioner state that in Claim 22 continuity did not specifically appear. Will you state whether the temperature there stated gives information as to whether that process necessarily operates as you state? A. Is claim 22 before your Honor?

The Court: Yes, I have it.

(Witness continuing) It states—"In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure". Under the temperature and pressure conditions there stated, it is inevitable that the ethyl chloride as formed will boil away and escape from the reaction bath, as soon as concentration has built up to a very small amount in the reaction bath. If the teaching of this claim is followed, it is therefore inevitable that the process must be operated as a continuous one
30 in the sense that the reagents are being supplied and
the product is being removed from the bath at the same time.

The Court: "Chlorinated lower aliphatic hydrocarbon" . . . what is a chlorinated lower aliphatic hydrocarbon? A. The adjective chlorinated means the element chlorine is present in the molecule. The hydrocarbon, strictly speaking, is a compound containing the elements of hydrogen and carbon only. That is how the name is derived.

The Court: Aliphatic?

A. Aliphatic is derived from a Greek word from which our word fat is also derived. The name was originally obtained from the fact that the substances which comprise animal and vegetable fats belong to this particular series. Perhaps the most convenient way of explaining the meaning of aliphatic is that the carbon atoms are attached to one another in a chain which may be branched or straight, but in any case not rings. When we encounter rings of carbon atoms—that is, for example, if we have five carbon atoms arranged in a position corresponding to the ends of my five fingers (witness illustrating) each one being in turn attached to two other carbon atoms in the ring, we no longer then have an aliphatic compound; that becomes a cyclic or ring compound.

31 Q. (By Mr. Wiles) Now, there are certain specific solvents mentioned. As I recall it tetrachloro-ethane is one of them. A. That is right.

Q. Is that one of the chlorinated aliphatic compounds? A. Yes, it is.

Q. Will you just draw the formula?

(Whereupon witness drew the formula.)

Q. Just write its name under it.

(Whereupon witness did as directed.)

Mr. Wiles: This is offered as Plaintiff's Exhibit 1.

(Whereupon the document above referred to marked Exhibit 1 by the reporter.)

Q. There (indicating) are the carbons in the end-to-end relation you spoke of, and then the hydrogens and chlorines. Tetra in that compound means four? A. Yes, sir.

The Court: Aliphatic—

(Witness interpolating) —chlorinated hydrocarbon, and one of the simpler ones. By simpler we mean one not containing many carbon atoms.

Q. (By Mr. Wiles) Aliphatic chains could be longer with more carbons? A. Yes.

Q. Now, I want you to take the Nutting process, which is primarily relied upon here, and first tell us how that
32 continuous type of process which is described in the
specification language, which has been disclaimed, was supposed to operate.

Mr. Wiles: I think with your Honor's permission, I will offer the certified copy of the file, which is a formal part of the proofs any way, as Plaintiff's Exhibit 2;

And the Disclaimer as Plaintiff's Exhibit #3.

(Whereupon the documents above referred to were marked Exhibits 2 and 3 by the Reporter.)

A. On page 2, line 4 of the Nutting patent, it is stated: "A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed". If the ethylidene chloride product is distilled, this then becomes a process which is formally analogous to the process in issue. The corresponding claim reads: "In a method of making ethylidene chloride"—

The Court (Interrupting): Claim 6?

Witness: Yes, Claim 6.

(Witness continuing) "In a method of making ethylidene chloride, the steps which consist in passing hydrogen chloride and vinyl chloride, simultaneously and at approximately atmospheric pressure, into a heated mixture of ethylidene chloride and a catalyst selected from the class consisting of aluminum chloride and ferric chloride, distilling ethylidene chloride from the mixture as it is formed, condensing ethylidene chloride from the distilled vapors, and returning any uncondensed vapors to the reaction."

33 It seems to me the language of the specification and
the claims is quite clear. This means a process involving some kind of a reactor in which we have the ethylidene chloride with the aluminum chloride, if that is the catalyst used, passing continuously the vinyl chloride, one reagent, and the hydrogen chloride the other reagent, and as ethylidene chloride is formed in the reactor it is removed by vaporization, boiling away at this temperature.

Q. (By Mr. Wiles) Now in comparing the process suggested by Nutting with the process here in controversy, in the Nutting process the raw material is vinyl chloride, in the other ethylene. I wish you would compare those two as to their analogy in a process of this kind. A. To a chemist somewhat unfamiliar with ethylene and vinyl chloride, it might seem that there is an extremely close analogy here. The only difference between ethylene and vinyl chloride, as far as structure and composition is concerned, is that vinyl chloride has a chlorine atom where ethylene has a hydrogen atom. The chemical and physical properties of vinyl chloride and ethylene are, however, widely dissimilar. In the first place, ethylene is uniquely unreactive among the simple olefines. It reacts more sluggishly toward practically every reagent which attaches itself to this double bond than is true of almost any other simple olefine. Vinyl chloride,
on the other hand, is just the opposite. The intro-
34 duction of that chlorine atom into the ethylene mole-
cule, converting it to vinyl chloride, changes the nature of the molecule to the extent that vinyl chloride is an extremely reactive substance. For example, vinyl chloride is used very widely for the manufacture of synthetic resins. The Goodrich Coroseal is a vinyl chloride product, produced from vinyl chloride, primarily, with small quantities of other substances presented by this phenomena which vinyl chloride shows, one molecule attaching itself to another molecule to form a larger one, which in turn attaches to another molecule of vinyl chloride, and so on until these extremely large molecules are formed which make up these synthetic resins.

The vinylite resins manufactured by the Carbide & Carbon Chemicals Corporation are made from vinyl chloride as the principal constituent. So the first essential difference between these two processes, as I view it, is that in the case of ethylene we have an extremely sluggish double bond, one which reacts with the greatest of difficulty; whereas in the case of vinyl chloride we have an extremely reactive double bond. Secondly, there is a considerable difference in boiling point between the ethyl chloride boiling at plus 12° C. which is produced when ethylene adds hydrogen chloride, and the ethylidene chloride boiling at 58° C., which is the compound formed when vinyl chloride adds HCl or

hydrogen chloride. This higher temperature of boil-
35 ing means that if the process is to be carried out
continuously at atmospheric pressure, as the claim specifies—

Q. (Mr. Wiles interrupting) The Nutting claim? A. Yes. (Witness continuing)—The Nutting claim specifies, Claim 6, which has been disclaimed, it is necessary to heat the reaction bath to a temperature above the boiling point of the ethylidene chloride, the boiling point being 58° C., which is a much higher temperature than is necessary to distill ethyl chloride from its reaction bath, ethyl chloride boiling at 12° C., 46° C lower than the boiling point of ethylidene chloride.

Now, the importance of this difference in boiling points consists in the reversibility of these hydrogen chloride additions. The addition of hydrogen chloride to ethylene or to vinyl chloride comes under the heading of what an organic or any chemist calls a reversible action. That means it is possible to start with the reaction products and produce from them the reagents used, and because of the nature of this reaction at higher temperatures, that reversibility becomes more and more important, so that if one goes to fairly high temperatures, not excessively high, it is possible to start with ethyl chloride, for example, and produce from it ethylene and hydrogen chloride by an exact reversal of the process in issue.

On the other hand, the same thing can happen with
36 ethylidene chloride. It is possible to heat that com-
pound and obtain from it hydrogen chloride and vinyl chloride. And because these reactions become more reversible as the temperature increases, the higher temperature necessitated, if we are to boil out the ethylidene chloride, becomes a matter of considerable importance. The most important difference in my judgment, however, between these two reactions which formerly seemed so analogous, is in the nature of the polymer produced. It is possible to polymerize ethylene in the presence of aluminum chloride. That has been done. The ethylene polymer when produced, however (and it is produced in very small quantities as this reaction proceeds) it is of a character resembling lubricating oil; it drains easily from the reaction vessel. The polymer from the vinyl chloride, on the other

hand, is a tarry, gummy, resinous material which does not drain out but which forms a pitchy, gummy material which plugs the reactor and prevents continuous operation from taking place.

To recapitulate then, there are, it seems to me, three essential differences here between these two apparently analogous reagents—

Firstly, the sluggish nature of ethylene towards polymerization compared to the very great ease of polymerization of vinyl chloride;

Secondly, the higher temperature necessitated by
37 the higher boiling point of ethylidene chloride as
compared to ethylene chloride; and

Thirdly, the nature of the polymer which is produced, which in the case of ethylene drains easily from the reaction vessel, whereas in the case of the vinyl chloride it is still gummy.

Q. Dr. Hass, you did not, as I understand it, take part in the tests of the Nutting process to determine if it was operative? A. No, sir, I did not.

Q. You knew of the results of those tests? A. Yes, sir. In fact, before the tests were run I stated the opinion that I believed they would come out in that way, for the reasons I have just indicated.

Q. In other words, from your knowledge as a chemist, and particularly specialized in the knowledge of this group of combines, you thought the Nutting process wouldn't work satisfactorily before you saw it tried? A. That is, the process of Claim 6? Yes, sir.

Q. I mean a continuous process. A. Yes, sir.

Q. And that was because you thought it would gum up? A. Yes, sir.

Q. Did the reversibility enter into that opinion too? A. Very greatly because in order for the vinyl chloride to polymerize it is necessary for the vinyl chloride to be there in
the reaction mixture. The greater the concentration
38 of vinyl chloride present, the greater the rate at which
a molecule can find another molecule of vinyl chloride
and attach itself to it. Therefore, the more reversible the reactions—that is, the greater amount of vinyl chloride present at equilibrium—the greater the change of polymerization of the vinyl chloride.

The Court: What is the formula for ethylidene? A. Ethylidene is a radical having—may I write it here, your Honor?

The Court: Yes.

(Witness writing, continuing)— two carbon atoms, one attached to three hydrogen atoms, the other attached to one hydrogen atom, and the other two valences of the one carbon atom being then left to attach themselves to anything else. In ethylidene chloride those two dashes on the right (indicating) representing valence bonds would be attached to two chlorine atoms. If it were ethylidene something else, those valences would be attached to something else.

Q. (By Mr. Wiles) Will you take that sketch, please, and complete it with the chlorines? Then label it and I will offer it in evidence.

(Whereupon the witness did as directed, and the exhibit was marked Plaintiff's Exhibit 4, by the reporter.)

The Court: And while you are doing that, will
39 you do the same thing for ethyl chloride?

Witness: Yes, sir.

(Whereupon the sketch was completed.)

Mr. Wiles: Now I think I would rather withdraw Dr. Hass, with my adversary's consent and let Mr. Amos demonstrate what was done with the process because those facts are part of Dr. Hass' evidence.

(Witness was thereupon withdrawn from the stand.)

James L. Amos, a witness called herein on behalf of the plaintiff, after first having been duly sworn by the Clerk, testified as follows:

Direct examination

By Mr. Wiles:

Q. Your name please? A. James Lawrence Amos.

Q. And what is your occupation? A. Research chemist, Physical Research Laboratory, The Dow Chemical Company.

Q. That is The Dow Chemical Company the plaintiff in this case? A. That is right.

Q. Are you acquainted, by the way, with Mr. Nutting? A. He lives in Midland.

Q. We have the application before the Court of this Nutting patent. Do you know whether or not those 40 processes have been worked out in the same laboratory or were they in different places? A. They were in different departments.

Q. So one might not know about the other's work at all? A. That is right.

Q. Now, were you sometime ago, in connection with this suit, requested to test out the Nutting process under various conditions suggested in that Nutting patent? A. Yes, sir.

Q. And have you made similar runs on the process here in suit making ethyl chloride? A. I have.

Q. Did you have something to do with the practical commercial development of that process? A. Yes, sir.

Q. What did you have to do with that? A. In my connections with The Dow Company I have done work on both the laboratory development and the semi-plant development on this continuous ethyl chloride process. In both instances the process was carried out by using anhydrous hydrochloric acid gas, anhydrous ethylene gas, and by passing the mixture of these two gases through a solvent bath containing chlorinated hydrocarbon solvent and an aluminum chloride catalyst. In the semi-plant development, the continuous unit was operated in this manner for periods of months without any trouble due to clogging or stoppage of the reactor by means of tars, gums, or other products pro- 41 duced by the reaction. This particular semi-plant produced 300 pounds a day of ethyl chloride continuously.

Q. That was under atmospheric pressure? A. That was operated at atmospheric pressure at a temperature slightly above 12° C., the boiling point of ethyl chloride.

Q. So the ethyl chloride distilled off as it was formed and condensed? A. That is right. Continuously.

Q. That semi-commercial plant, half, was that what you meant by semi? A. That is right. Half size.

Q. That plant followed the steps of Claim 22 which you are familiar with? A. Yes, sir.

Q. Now, prior to that, you had run the same ethyl chloride process on a laboratory scale in glass? A. Yes, sir.

Q. Now when you came to run this Nutting process that was done, as I understand it, in glass, was it not? A. Yes, sir.

Q. Laboratory scale? A. Yes, sir.

Q. Does the photograph I now show you illustrate the apparatus that you used (handing same to witness)? A. Yes, sir.

(The photograph was thereupon marked Exhibit 5 by the Reporter.)

42 Q. I wish you would please describe that apparatus and how the flow took place through it. A. The apparatus used for the continuous production of ethylidene chloride from vinyl chloride and anhydrous hydrochloric acid as described by the Nutting patent, consisted first of a hydrochloric acid generator. The hydrochloric acid was generated by means of sodium chloride, commonly called table salt, and concentrated sulphuric acid, the two compounds reacted in a glass flask and produced the hydrochloric acid gas. The resultant gas which was evolved was dried by passage through a tube containing anhydrous calcium chloride, which removed the water. The resultant substantially dry hydrochloric acid was fed through a calibrated flowmeter, as indicated by the label on this photograph.

The vinyl chloride used in these experiments was a highly purified grade of vinyl chloride, the type used in the plastic trade. This compound, that is the vinyl chloride, was fed in vapor state through a calibrated flowmeter and the vinyl chloride flow and the hydrochloric acid gas were premixed prior to entry into the base of the glass reactor. The glass reactor consisted of a Pyrex glass tube 1½ x 30″, one-half the height packed with ¼″ glass rings.

Q. What is the purpose of those rings, please? A. The purpose of the rings is to give good distribution in mixing of the reactants in the solvent bath containing the aluminum chloride catalyst. 43

Q. That is a common procedure for that purpose, is it? A. That is right. On continuous processes they use equipment of this type in commercial operation.

(Witness continuing) The reactor contained the chlorinated hydrocarbon solvent into which was suspended and dissolved the aluminum chloride catalyst. The entire reactor was placed inside a 3″ glass test tube water bath which facilitated the heating of the reactor.

The passage of the hydrochloric acid and vinyl chloride mixture up through the chlorinated solvent bath and aluminum chloride mixture resulted in the reaction, which consisted in the production of some ethylidene chloride, which boiled off at a temperature above the boiling point of ethylidene chloride (that is 58° C. thereabouts and came off at the top of the reactor at substantially atmospheric pressure and entered a water-cooled condenser from which flowed the condensed ethylidene chloride into a receiver, as noted in the photograph.

From the receiver a line carried the reacted hydrochloric and other gaseous products to the hydrochloric acid scrubber, which consisted of a vertical tube packed with glass beads, down through which flowed hot water. The hot water was reacted with the hydrochloric acid and formed aqueous hydrochloric, thereby removing it from the gaseous mixture.

44 The scrubber was operated hot so as to prevent condensation of vinyl chloride or other materials in the mixture. The gases coming from the top of this hydrochloric acid scrubber passed through a calcium chloride drying tube, which removed the water from the gases, into a vinyl chloride receiver which, in turn, was cooled by a dry ice, chloroform, carbon tetrachloride mixture. During the operation of this process the reactor at all times was maintained at approximately atmospheric pressure.

Q. Now, is that about the same type of apparatus that you would use in the process here in controversy? A. Yes, sir.

Q. You would use that same apparatus and simply put in ethylene gas in place of vinyl chloride? A. That is right.

Q. And then it would run right along and produce ethyl chloride? A. Yes. However, you would have to operate under different physical conditions. The apparatus would be the same.

Q. Pressure would be the same A. Pressure would be the same, yes.

Q. The temperature would vary because you would have to fit the boiling point to the particular thing you make? A. Yes, sir.

Q. Now, in operating this Nutting idea, did you use different baths, different solvents? A. Yes, sir.

45 Q. Did you use the particular one specifically specified by Nutting to make ethylidene chloride? A. Yes, sir.

Q. Did you also use the bath that is referred to in the application here in controversy, tetrachloro-ethane? A. Yes, sir.

Q. Now, I wish you would tell the Court just what happened when you ran these so-called Nutting runs. Suppose you take up Run 7. That is typical of them all in a general way, is it not? A. (Witness referred to records) Yes, sir.

Q. I am just taking that one at random. Suppose you take that one and describe to the Court what you put in and what you got out. What happened to the apparatus and how soon? You have prepared a tabulation of your results, have you not? A. Yes, sir. (Witness handed tabulation to counsel.)

Mr. Wiles: I want one for my adversary.

(Whereupon Mr. Kelly was handed tabulation.)

(Witness continuing) In Run 7, which was carried out in the apparatus just described, 200 grams of ethylidene chloride was placed into the reactor as a solvent.

Q. In that case, as recommended by Nutting, the solvent and the final end product are the same thing, are they not? A. Yes, sir. To this was added 5 grams anhydrous powdered aluminum chloride. Into this mixture was passed 185 grams of vinyl chloride, 110 grams of anhydrous
46 hydrochloric acid gas at a uniform rate over a period
of four hours, while the reactor was maintained at approximately atmospheric pressure and at a temperature varying from 28 to 53° C. After operating 4 hours, 99.2 grams of ethylidene chloride was produced from the vinyl chloride and hydrochloric acid passed into the reactor. At the same time 44.2 grams of tarry, black residue was produced. The percent of the total vinyl chloride which was passed through the reactor and which was converted to ethylidene chloride was only 33.8% as compared to the continuous ethyl chloride process of 90 to 95%.

The percent of the vinyl chloride used in the reaction—that is, used up and transferred to ethylidene chloride, was only 53.5% as compared to the ethyl chloride process of 90 to 95%. The percent vinyl chloride not recovered as vinyl chloride from the products coming from the reactor or as ethylidene chloride, was 29.5%. In other words, 29½% of the vinyl chloride did not go to either ethylidene chloride or was recovered as unreacted vinyl chloride.

Q. What did become of that? A. The majority of that material polymerized. It polymerized to the black, thick residue which deposited on the rings of the reactor. (Witness continuing) After four hours of operation, the rings of the reactor were coated with a black, tarry residue, resulting from the polymerization of the vinyl chloride. During this operation it was necessary to maintain the 47 temperatures of the reactor below the boiling point of the ethylidene chloride because of the violent reaction between the vinyl chloride and the hydrochloric acid. It would tend to boil the entire liquid contents of the reactor over into the receiver. That is the reason for the operation at 28-53° C.

Q. So that in that process you made only about 30% of your vinyl chloride into the products you wanted? A. Yes, sir.

Q. And you made almost as much into this black tar? A. Yes, sir.

Q. At the end of the four hour operation was the apparatus in fit condition to continue? A. No, sir.

Q. Have you brought the reactor here that you used in that run? A. Yes, sir.

Q. Will you produce it, please, and show it to the Court?

(Witness produced reactor.)

A. This is the reactor in which Run 7 just described was operated. The mixed gases of hydrochloric acid and vinyl chloride passed through this entrance tube into the base of this reactor (illustrating) up through the beads which were submerged in the ethylidene chloride solvent containing the aluminum chloride catalyst. Prior to the addition of the aluminum chloride the ethylidene chloride solvent 48 was water clear, but after four hours of operation the tower resulted in this condition (indicating). The tarry material is visible as one looks through the glass. It ran down the sides and deposited here (pointing) when the reactor was placed in a horizontal position. After four hours' operation all the rings were firmly set together.

Q. And is that so plugged that further operation would not have been possible? A. It is. Usually it plugs at the entrance of the gaseous materials into the reactor—that is, of course, the highest concentration of the reactants would occur in the bottom part of the tower. Of course the worse plugging of this tower is at the bottom, which in turn prevents, of course, the entrance of vinyl chloride and hydrochloric acid gas.

The Court: We will recess until 1:30 o'clock.

(Whereupon at 12:30 o'clock p. m., a recess was taken until 1:30 o'clock of the same day.)

49 Washington, D. C.,
Wednesday, June 12, 1940.
1:30 o'clock p.m.

The taking of testimony in this cause was resumed pursuant to recess.

Parties present as before.

James L. Amos, witness herein, having previously been sworn, resumed the stand and testified further as follows:

Direct Examination

By Mr. Wiles:

Q. Mr. Amos, I think you finished the discussion of your Run #7 before the luncheon recess, did you not? A. Yes, sir.

Q. Now in your run which you numbered 8, as I understand it there you used the same type of solvent that is used in the application here before the Court? A. That is right. That is Run 8?

Mr. Wiles:

A. Yes, sir.

Q. Now describe the results that you got there. A. On run 8 the same type of apparatus was used. However, in this run 300 grams of tetrachloro-ethane was used as the solvent in the bath in the place of ethylidene chloride which was used in run 7. The amount of aluminum chloride used was 7½ grams, the amount of vinyl chloride passed in

50 to the reactor was 211 grams; grams of hydrochloric acid gas, anhydrous, 130 grams. These two reactants were fed at a uniform rate for a period of 4½ hours while maintaining the reactor at a pressure slightly above atmospheric and at a temperature ranging from 29 to 71° C. The results of this experiment are 142.9 grams of ethylene chloride was produced, 43 grams of tarry residue was produced, the percent of the total vinyl chloride passed through the reactor converted to ethylidene chloride was 42.7%. The percent of the total vinyl chloride used up in this reaction and of that amount which went to ethylidene chloride was 65.2%. That is, the amount of vinyl chloride used up in forming ethylidene chloride was 65% of the total vinyl chloride consumed. The percent vinyl chloride unaccounted for as recovered vinyl chloride or as ethylidene chloride in the products we were after was 22.8%.

Q. That went into the residue? A. That is right.

(Witness continuing) Again the reason for operating the reactor at 29 to 71° C. was that the reaction was so violent that the temperature had to be kept down to prevent the boiling of the solvent in the reactor and all of the material over into the receiver, the ethylidene chloride receiver.

51 Q. When that run was over at the end of 4½ hours, what was the condition of the reactor? A. The reactor after 4½ hours' operation as outlined in Run 8 showed that the glass rings in the reactor were coated with a heavy tarry material and the rings at the bottom of the tower were cemented together with a tarry residue.

Q. Was it possible to continue that run any longer? A. No, sir, the bottom part of the tower was plugged with a tarry residue resulting from the reaction.

Q. Now, Mr. Amos, we have set up some apparatus here.

Mr. Wiles: We wanted to get it started, your Honor, so we wouldn't consume any extra time even though we break the continuity of the testimony.

Q. (Continuing) This is intended to designate, is it, the instability of the end product, ethylidene cloride as compared with ethyl chloride? A. Yes, sir.

Q. And that ethyl chloride is stable in the presence of an aluminum chloride and will maintain itself for a long time without any change under operating temperatures for this process? A. Yes, sir.

Q. Whereas ethylidene chloride is the reverse reaction of this formula and is partially transformed into hydrochloric acid which boils off, is that correct? A. Yes, sir.

52 Q. Now, you have two sets of apparatus exactly alike here. The one on the right as judged from the bench, has ethylidene chloride in it, has it not? A. Yes, sir.

Q. And is that a pure grade? A. That is a pure grade of ethylidene chloride, produced by the Eastman Kodak Company.

Q. And in the other flask you have ethyl chloride? A. Yes, sir.

Q. In each flask there is a condenser, is there not? A. That is essentially correct, yes.

Q. The permanent gas such as hydrochloric acid will go out of the reflux condenser down through this tube (indicating) and will bubble through these bubble-like columns? A. Yes, sir.

Q. And these bubble columns are filled with alkali, are they? A. It is a dilute caustic solution containing phenolphthalein indicator which on the alkaline side produces the red color. Upon neutralization or consumption of the caustic, the red color will disappear, indicating that an acid has been produced, which consumes the caustic in the water.

Mr. Wiles: Now as yet the aluminum chloride hasn't been put into either one of these flasks. We are about to add that now.

53 Q. Now, these two flasks when the aluminum chloride is added will represent the end product of these two processes, the Nutting and the one here in controversy, with the catalystic agent that is actually in the reactor? A. Yes, sir.

(Whereupon material was added to both flasks.)

Q. Now that one there, the one to the right, facing the Court, is the one which is instable? A. That is the ethylidene chloride, that is true.

Q. Which with the aluminumum chloride will be changed? A. Yes, sir.

Q. In ordinary room temperatures these products will boil, will they not? A. Ethyl chloride will boil at 12°. In other words, it will boil at room conditions. The ethylidene chloride boils at 58°, which is above the ordinary room temperature.

Q. But if it decomposes, giving off gas, the gas will come off? A. Yes, sir.

Q. Now, I have here a sample which is marked "Sample of Residue Run #5". That run is not listed in the table you have prepared, but will you tell us how that residue compares with the residue that was made in the other runs? That is, in character. A. This residue in Run 5 resulted from the continuous operation for the production of ethylidene chloride as described in Nutting's patent where-
54 by ethylidene chloride was used as a solvent in the
bath in the presence of aluminum chloride during the passage, continuously, of vinyl chloride and anhydrous hydrochloric acid. This residue is a sample of the tarry material from the reactor zone which is similar to the tarry material as described in Run 7 previously. It is this tarry material which cements and plugs the glass rings in the reactor.

Q. Now, I want to shorten this as much as I can. Some of these runs that you have listed here are practically duplicates, are they not? A. Yes, sir.

Q. Run 11 was a special kind of a run, was it not? A. Yes, sir.

Q. Will you describe that one? A. Run 11 was made in the same type of apparatus as used in the preceding runs. In the reactor was placed 300 grams of ethylidene chloride and 7½ grams of aluminum chloride. No vinyl chloride or anhydrous hydrochloric gas was passed through the reactor. The purpose of the run was primarily to show the effects of aluminum chloride upon the ethylidene chloride solvent at the physical conditions—that is, temperature and pressure which was used in the other runs already described. In this particular run the temperature was gradually raised from 21° to 60° C. Again, the rea-
55 son for that was that even at 21° C. the reaction be-
tween aluminum chloride and the ethylidene chloride which decomposed ethylidene chloride to hydrochloric acid and vinyl chloride, as well as a tarry residue as described, was so violent that if the temperature wasn't kept down or lowered the entire contents of the reactor would have boiled over into the receiver. The duration of the run was 4½ hours—4.58, to be exact, and during that time 14 grams of hydrochloric acid was developed as a gas from the reactor;

8.87 grams of vinyl chloride was recovered from the reactor. In other words, ethylidene chloride decomposed and 8.87 grams of vinyl chloride was recovered.

Q. That is the first product, the Nutting end product, is going back to its original constituents? A. Yes, sir.

Q. Referring now particularly to the right apparatus set up here, is that same decomposition now taking place in the ethylidene chloride that is in the flask? A. Yes, sir.

Q. And is that demonstrated in part by the change in color? A. Yes, sir.

Q. That reddish color we now have is some of this gummy material starting to form? A. That is right.

56 Q. I don't mean in the bubble—I mean in the reaction flask. A. Yes, sir.

Q. And the gas coming out first displaces air in the apparatus but the bubbles passing out there are equivalent in amount to the hydochloric acid gas that has been broken off? A. Yes, sir.

Q. Vinyl chloride is polymerizing to start to form a gum? A. Yes, sir.

Q. If it were warmer it would go very much faster? A. Yes, sir.

Q. Now, going back to this run 11, as I understand it you were carrying on there at somewhat higher temperatures precisely the thing you were carrying on in the apparatus to the right before the court? A. Yes, sir.

Q. The decomposition of the end product back to the things that Nutting started? A. Yes, sir.

Q. Is this the reactor that you used in that run (indicating)? A. Yes, sir, this is the reactor for Run 11.

(Whereupon the Reactor Run #7 was marked Plaintiff's Exhibit 6 by the Reporter, and Reactor Run #11 was marked Plaintiff's Exhibit 7.)

Q. I just want to ask one or two more questions. You are familiar with that part of the Nutting patent which was stricken out by the Disclaimer? It says: "A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed".

57 Q. Now from your experience with these runs, do you consider that a continuous process? A. No, sir.

Q. The best runs you were able to get were a very few hours during which time you made practically as much gum as you did product, is that right? A. That is on conversion, yes.

Q. It also says that the quantity of catalyst required to produce a given quantity of product is reduced materially. Is that true? A. No, sir.

Q. In fact it is exactly the opposite, is it not? A. Yes, sir.

Q. Now this Nutting patent describes outside of that paragraph a number of processes? A. Yes, sir.

Q. Those are perfectly satisfactory processes, are they not? A. Yes, sir.

Q. The continuity in here does not work? A. Yes, sir.

Mr. Wiles: I think that is all.

Your witness.

Cross Examination

By Mr. Kelly:

Q. Just a couple of questions I have, your Honor. These two processes here that are demonstrated, are they the 58 complete process as described in the plaintiff's application? A. These two units?

Q. That one (indicating one to the left) according to plaintiff's application? A. No, sir. These two units, the primary purpose of this experiment is to show the stability of these two chlorinated aliphatic hydrocarbons in the presence of aluminum chloride.

Q. Well, in this setup here, would it make any difference if you included a solvent in there other than the reaction product? A. No, sir.

Q. And passed gas through? A. You would still obtain the decomposition of ethylidene chloride.

Q. There is no solvent suggested by Nutting that would tend to retard the formation of that syrupy or gummy substance. A. No, sir. However, by using a chlorinated hydocarbon solvent boiling at a temperature higher than ethylidene chloride, it necessitates operations at a temperature higher than 58° C. for continuous removal of ethylidene chloride, thereby accelerating the decomposition of the ethylidene chloride by aluminum chloride. In other words, the higher the temperature of operation, the worse the decomposition of your final product, and of course polymerization of the final chloride to the gum.

59 Q. I call your attention to the statement in the Nutting patent appearing on page 1, column 1, lines 23, 24, 25 . . . "Furthermore, the syrupy mass which is formed frequently interferes with or stops the gas flow . . .". There, of course, as you know, he was referring to another patent before the syrupy mass was formed? A. Yes, sir.

Q. Would that put a person expert in the art on notice you might look out for a syrupy mass or do something about it?

Mr. Wiles: What was that question?

(Whereupon the question was read by the Reporter.)

A. I would say no, particularly as he doesn't define what a syrupy mass is. The use of aluminum chloride as a catalyst in some process if not operated under proper conditions will produce syrupy masses. For example, water will do it. If you have a chlorinated solvent containing aluminum chloride and you allow water to get in, you will obtain a syrupy mass. In other words, there are different types of syrupy masses; he does not define what his syrupy mass is.

Q. Suppose I put the question this way—In view of the fact the Nutting patent calls attention to the formation of an objectionable material in the reactant column, would put that a person on notice that he might expect such a thing or would he be surprised when he found it? A. I would
60 say he would be surprised to find it if he practiced
Nutting's patent as he outlines it, because Nutting stipulates anhydrous conditions.

Q. Even though Nutting says that you would get a syrupy mass by following this other process? A. I would say on that question that studying the process as outlined by Nutting's examples, that the answer would be no.

Q. You would not expect that? A. That is right, because I think it would follow in his process as in the body. As I recall he points that out. Page 1, first column, lines 29, 30, through 34—"We have now found that by carrying the reaction out in a non-aqueous liquid medium, rather than in vapor phase, the yield of ethylidene chloride is increased considerably, by-product formation is reduced, and the attendant operating difficulty mentioned above is avoided." So by knowing that, you certainly would be surprised to discover this condition which we illustrated with this experiment.

Q. Even though he says it would be reduced, he does not say it would be abolished. A. However, he does state that "the attendant operating difficulty mentioned above is avoided". That is, the difficulty of the plugging of the reactor so you would have stoppage of gas flow, which very obviously would prevent the process from being continuous.

61 Q. Well, you revealed that in runs 7 and 8 according to your finding, there is substantial production of the reaction product. A. May I have that question please?

Q. In your runs 7 and 8 did Nutting et al. patent produce a substantial yield of the reaction product there? A. No, sir. When one compares runs 7 and 8 continuous operation to the examples of batch operation as cited by Nutting's patent, one will note that the Nutting yields are approximately twice those cited in runs 7 and 8.

Q. What was the yield in run 7, for instance? A. The yield in Run 7 was 53½%.

Q. That is not substantial? A. Not commercially, no.

Q. In run 8, what was the yield? A. Run 8, the yield was 65.2%.

Q. Is that substantial? A. Commercially no.

Q. The run in this case would it have to be a commercial success to be a considerable quality?

Mr. Wiles: I think that is a conclusion.

Witness: I can answer that question. May I?

Mr. Wiles: I judge so.

A. With the knowledge of Nutting's batch process of yields better than 90%, a batch process of that type would be far more commercial and economical than a
62 continuous process operating at 53½ or 65.2% yields.

Mr. Kelly: That is all.

Redirect examination

By Mr. Wiles:

Q. I want you to explain how you use the term "yield and conversion". A. For example, in Run 7 the percent conversion is given as 33.8%. That figure represents the percent of the total vinyl chloride passed through the reactor that went to ethylidene chloride.

Q. In other words, that is the ultimate amount of end product produced, based on what you put in it? A. That is right.

Q. Now, you have given yield in percent. What does that mean? A. The percent yield is the percentage amount of the vinyl chloride used up. What I mean by "used up" is the amount of vinyl chloride used up and producing the ethylidene chloride. That is based on the amount of vinyl chloride consumed in both the ethylidene chloride production and the tarry residue production. In other words, you would take the amount of vinyl chloride used in the ethylidene chloride production and divide that weight by the summation of the weight of vinyl chloride used in ethylidene chloride plus the vinyl chloride which went to tars. And that times 100 gives your percent yield.

63 Q. Now I want to get the distinction. As I understand it, the percent conversion is the percent of end product you got based on what you put in? A. Yes, sir, that is based on the total through-put of the raw material, one pass; one passage through.

Q. The other, the so-called yield, would take into account such vinyl chloride as went through and was recovered as vinyl chloride on the other side? A. That is true. In other words, you take credit for the vinyl chloride you recover as such. It is in the products. That is the reason why the yield figure is higher than the conversion figure, because you have credited yourself with the vinyl chloride which did not react and is recovered as vinyl chloride.

Q. Whereas in run 7 you only got 33.8% in your final product, a considerable amount of vinyl chloride went through without anything happening to it? A. Yes, sir.

Q. So the 53% is where the vinyl chloride disappeared in the process somewhere? A. The 53% as noted as the percent yield, is the percent of the total vinyl chloride used which was converted over to ethylidene chloride. In other words, approximately 50%, or half of the vinyl chloride, consumed, used up, went to the desired product—ethylidene chloride.

Q. The rest of it went mostly to tar? A. Only the
64 percent that went to tar was approximately 29½%.

Mr. Wiles: I think we can call attention now to the fact that this has now forced the air out of the apparatus on the right and the hydrochloric acid formed is beginning to come through and has turned this liquid from red to white. You will notice, your Honor, the first is losing its color. As more acid comes down you will observe one of these beads after another will go white.

That is all.

Henry B. Hass, witness herein, having previously been sworn, resumed the stand and testified further as follows:

Direct examination

By Mr. Wiles:

Q. Now, Dr. Hass, you have heard the testimony of Mr. Amos about these runs? A. Yes, sir.

Q. Are the tarry materials that he produced here and illustrated the sample of the type of product you were testifying about as commonly formed in the polymerization of vinyl chloride? A. That question requires a qualification. When vinyl chloride is polermized commercially for the production of these synthetic resins, it is substantially a colorless
65 product which is different from what we are talking
about here. This tar in the bottle before his Honor is the type of thing I was referring to this morning as being formed as a by-product of this reaction. That is similar to but yet very different from the desirable vinyl chloride polymers which are formed commercially and intentionally.

Q. Now, were you familiar with the Curme patent prior to being consulted about this case? A. Yes, sir. I teach a course at Purdue which I call the Chemistry of Petroleum Derivatives. In that course we went over this Curme process in class every time the course was given.

Q. Is Curme a well-known, eminent chemist? A. Curme is one of the most outstanding chemists in this field in the country. He, more than any one man, is responsible for the Carbide & Carbon Chemicals Corporation phenomenal development, which is one of the proud achievements of American chemistry.

Q. Now in your study of the Curme patent, what do you understand to be operating conditions that he describes for getting this reaction of hydrochloric acid? A. Curme states for commercial yields both high pressure and catalysts are necessary.

Q. Now, in its opinion the Board said:

> "There (the plaintiff's main contention is that Curme indicates that high pressures are necessary. It is our view that Curme has no such teaching when a catalyst is used. See Lines 52 to 54, page 1 of Curme."

Does your understanding of this as a chemist
66 agree with that opinion? A. No, it does not. My
feeling about the Curme patent has always been it leads one directly to the use of high pressure.

Q. In the language of the patent—"Pressures up to 160 atmospheres, without a catalyst, and aluminum chloride as a catalyst, without pressure, have each been tried" . . . and he says . . . "In either case ethyl chloride is produced in substantial quantity". Do you understand that one runs that process without pressure? A. If one stops there, you might so conclude but not the entire patent.

Q. And when you come to its claims, every claim calls both for catalyst and pressure, does it not? A. I want to check that by referring to the patent. (Witness looked through patent.) Yes, that is correct.

Q. Now, what did you gather when you read the matter immediately following that which the Board cited, beginning line 55 of page 1? A. "The best method for producing ethyl chloride employs both a catalyst and pressure. In the presence of aluminum chloride and at pressures no higher than 35 atmospheres, commercial yields are obtainable, even at room temperature". That indicates to me that Curme was trying to teach that the desirable operating conditions and the only ones worth covering in the claims, the only practical
ones, were those using super-atmospheric pressure.
67 Perhaps it might be desirable here to point out
some of the laws of chemistry in regard to pressure. I think it is a theoretically sound conclusion any reaction which occurs at super-atmospheric pressure will occur to

some extent at atmospheric pressure. The difference there is that the amount of reaction may be so slight as to be wholly impractical at atmospheric pressure, whereas at super-atmospheric pressure the amount of the desired reaction may be very great and commercially feasible. With that law of chemistry in mind, a skilled chemist reading this would assume that Curme had concluded that this process when operated at atmospheric pressure does not give commercially desirable results.

Q. Now, being fully familiar with the Curme patent, and taking it up with your classes before you had anything to do with this litigation at all, what impression was made on you when you discovered by conference with representatives of the Dow Company that they were actually making ethyl chloride at atmospheric pressures? A. I was distinctly astonished to realize that Curme had, in the vernacular, "missed the boat". When one deals with such a substance as hydrogen chloride, which under many conditions is corrosive, it is undesirable to work at super-atmospheric pressure if that can be avoided. Curme if one of our very
68 best chemists. To think that he had been the pioneer
in this field, had worked out a process which seemed very logical, and then to learn that someone coming later had found much more desirable conditions for carrying out this reaction, gave me a very distinct sensation of surprise.

Q. Now, if you take the disclosure of Nutting, is there anything there that would lead you as a chemist to try the thing on the ethylene reaction to make ethyl chloride? A. Just to the contrary. Ethylene being the most sluggishly reacting of all the simple olefines, vinyl chloride having as its outstanding characteristic its ease of adding to other molecules, I would conclude that a set of conditions suitable for vinyl chloride would in all probability be unsuitable for reaction with ethylene.

Q. The one wouldn't lead you to try the other? A. The one would lead me directly away from the other.

Q. Now, I wish you would state, as a skilled chemist, whether in Nutting alone or Nutting and Curme together, there is anything which would lead you directly and immediately to the process of the application here involved and which you have described so clearly and certainly there would be no necessity for experiment? A. No, indeed.

69 Q. Now, in view of your experience in the preparation of compounds like ethylidene chloride, if you wanted to make ethyl chloride and you saw the Nutting and Curme patents, would you be led irresistibly to the conclusion you had only to substitute ethylene for vinyl chloride in Nutting and arrive at the process described here? A. Absolutely not. To begin with, the three reasons I mentioned this morning, namely that ethylene is a sluggish olefine whereas vinyl chloride is a very reactive chlorinated compound; the higher boiling point required to boil off the ethylene chloride as it is being formed; the ease of polymerization of vinyl chloride, formation of semi-gums there. And in addition, the teaching of Curme as clearly implied in this patent that the only practical way of doing it is at super-atmospheric pressure would lead one, I should say, away from the process in issue.

Mr. Wiles: Now, may I call attention to the fact the first two or three of those bubbling chambers have now changed to white?

The Witness: I am not sure his Honor can see it.

The Court: I can see it.

Mr. Wiles (continuing): That means enough hydrochloric acid has been liberated by decomposition of ethylidene chloride to neutralize the caustic in the first bead or
enlargement of the tube, and also the air spaces in the
70 apparatus in which the air had to be pushed out in
the first place.

Witness: Substantially that is true. There is still some air in the apparatus, as can be noticed by the bubbles passing through the apparatus. Enough air has been expelled so a considerable amount of hydrogen chloride is coming off with the air.

Q. The other one, both running the same time, the ethyl chloride is boiling right along and dripping back, is it not? A. Yes.

Q. And there has been no decomposition of any kind, as indicated by the fact no gas has passed out of the apparatus? A. Well, absolutes in chemistry are relatively rare. I would like to qualify that by saying not more than a negligible amount of decomposition has occurred.

Q. If any appreciable amount, you would have had some bubbles coming out? A. Yes, the bubbles would have been passing through the red liquid in the absorption apparatus.

Mr. Wiles: Your witness.

Cross Examination by Mr. Kelly:

Q. Dr. Hass, you say you are familiar with the Nutting et al. patent? A. Yes, sir.

71 Q. Do you have a copy of it? A. I do not.

(Whereupon counsel handed one to witness.)

Q. Does that patent disclose the use of any chlorinated lower aliphatic hydrocarbons as a solvent in the reaction bath? A. On page 1, line 49 and following, it states: "The liquified reactant, vinyl chloride, or the product, ethylidene chloride, is preferably employed as the reaction medium". Those are both simple chlorinated aliphatic compounds.

Q. How about the ones at the bottom of the line of that column? A. It states: "However, other non-reactive solvents, e.g. trichloroethane, acetylene tetrachloride, etc., may be employed, if desired."

The Court: What are you reading from?

Witness: Nutting patent, page 1, line 55 and following. Bottom of the first column and top of the second.

Q. (By Mr. Kelly) The last line, page 1, column 2, discloses the use of naptha, trichloro-ethane, acetylene tetrachloride, ethylidene chloride, etc. Were any of those chlorinated lower aliphatic hydrocarbons? A. Yes, all of those except naptha.

72 Mr. Kelly: That is all.

Mr. Wiles: That is our case.

Mr. Kelly: I would like to offer in evidence the folder as Defendant's Exhibit 1, containing these references.

(Whereupon the document was marked Defendant's Exhibit 1 by the reporter.)

Mr. Kelly: There were some of the plaintiff's exhibits I didn't understand as being offered. There were two sketches we haven't seen.

Mr. Wiles: I handed them up as they were marked. I do so now offer them as exhibits. I intended to offer all exhibits as they were handed up.

The Court: I so understood.

Mr. Wiles: What is your practice, your Honor? Do you want briefs?

The Court: I prefer it. My knowledge of chemistry is so limited I will have to take the record.

(Thereupon at 2:35 o'clock p.m., an adjournment was taken.)

73 *Order Re Exhibits*

Filed November 18 1940

* * *

It is hereby ordered this 18th day of November, 1940, that the original exhibits of both parties made of record in this cause may be taken to the United States Court of Appeals for the District of Columbia for use in connection with the appeal herein to that court.

JENNINGS BAILEY
Justice

Entry of the above order is without objection on the part of Defendant

W. W. COCHRAN
Counsel for Defendant.

74 *Memorandum of Court*

Filed June 25 1940

* * *

I agree with the Board of Appeals of the Patent Office in rejecting the plaintiff's claims upon the Curme and the Nutting et al. references.

The complaint should be dismissed with costs.

BAILEY
J.

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75 *Findings of Fact*

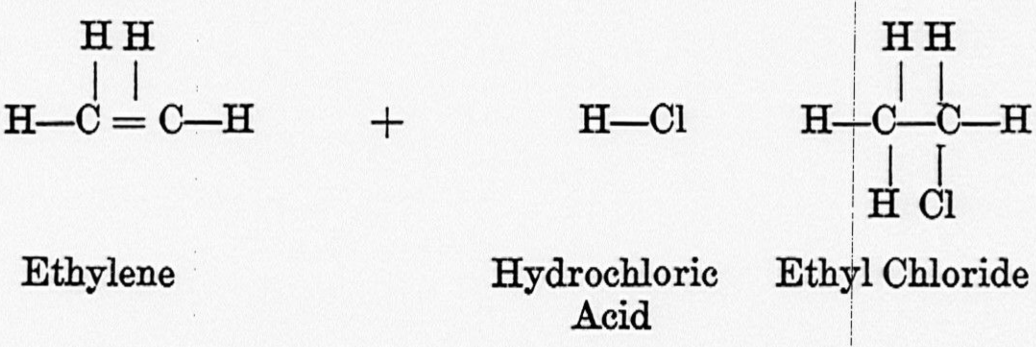
Filed October 1-1940

* * *

1. In this action brought under the provisions of Section 4915 Revised Statutes (U. S. C. Title 35, Sec. 63) it was

sought to have the Commissioner of Patents authorized to issue to The Dow Chemical Company a patent on the application of Edgar C. Britton, Jack L. Williams and Carl F. Prutton, Ser. No. 44,252, filed October 9, 1935, containing claims 22 to 34, inclusive, as set out in Paragraph 7 of the Complaint.

2. The application of Britton, Williams and Prutton in suit discloses a continuous process of making ethyl chloride. In this process there is provided a liquid reaction bath of a chlorinated lower aliphatic hydrocarbon, preferably tetrachlorethane, and an aluminum chloride catalyst. Gaseous ethylene, an unsaturated hydrocarbon with a double bond, and dry hydrochloric acid gas are mixed and bubbled into the bath which is at atmospheric pressure and somewhat above 12° C., the boiling point of ethyl chloride, the desired end product. Aided by the aluminum chloride catalyst, the hydrochloric acid decomposes and its two atoms attach themselves to the ethylene at the double bond according to the reaction



$$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}H} \quad + \quad \mathrm{H{-}Cl} \quad \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{Cl}{\overset{H}{C}}{-}H}$$

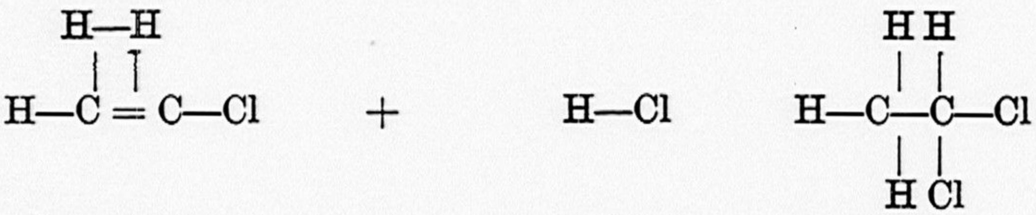
The ethyl chloride boils off as fast as it is formed, because the temperature of the bath is above the boiling point of ethyl chloride, and is condensed and freed of any part of the bath liquid which may have been carried off with it. The process has been run continuously for months at a
76 time without trouble and without gumming up the apparatus; and during such time a production of ethyl chloride to the amount of 90% to 95% of that theoretically possible from the raw materials fed to the bath has been obtained. The process is simple, inexpensive and efficient

3. The patent to Curme, 1,518,182, discloses a process of making ethyl chloride by reacting ethylene and hydrogen chloride in a reaction bath containing aluminum chloride

as a catalyst. The specification states that the process may be carried out without pressure and at room temperature.

4. The patent to Nutting, et al., 2,007,144, discloses a continuous process of making ethylidene chloride by passing vinyl chloride and hydrogen chloride into a liquid reaction bath. This bath is made up of a chlorinated lower aliphatic hydrocarbon and aluminum chloride as a catalyst. This bath is maintained at a temperature above 12° C., but below its own boiling temperature, and under approximately atmospheric pressure.

The reaction is



$$\begin{array}{c} \mathrm{H{-}H} \\ |\quad | \\ \mathrm{H{-}C{=}C{-}Cl} \end{array} \quad + \quad \mathrm{H{-}Cl} \quad \begin{array}{c} \mathrm{H\ H} \\ |\ \ | \\ \mathrm{H{-}C{-}C{-}Cl} \\ |\ \ | \\ \mathrm{H\ Cl} \end{array}$$

Vinyl Chloride | Hydrochloric Acid | Ethylidene Chloride

5. The Nutting, et al. patent discloses an operative continuous process for the production of ethylidine chloride.

JENNINGS BAILEY,
Justice.

77 *Conclusions of Law*

1. It was not invention to use a chlorinated lower aliphatic hydrocarbon as the reaction solvent, or to carry out the process of the patent to Curme 1,518,182, continuously, in view of the patent to Nutting 2,007,144.

2. It was not invention to use the process disclosed by the patent to Nutting, et al. to produce ethyl chloride in view of the patent to Curme 1,518,182.

3. Claims 22 to 34, inclusive, of the application in suit are not patentable over the prior art.

4. Plaintiff is not entitled to a patent on the application of Edgar C. Britton, et al., Ser. No. 44,252, in suit, containing any of Claims 22 to 34, inclusive.

5. The complaint should be dismissed.

JENNINGS BAILEY
Justice

78 *Judgment*

Filed October 1-1940

* * *

This action came on to be heard at this term; and thereupon upon consideration thereof, it is this first day of October 1940, adjudged as follows:

That the Complaint in this case be, and it is hereby, dismissed with costs against the plaintiff.

JENNINGS BAILEY.
Justice

79 *Notice of Appeal*

Filed October 19 1940

* * *

Notice is hereby given this 19″ day of October, 1940, that The Dow Chemical Company hereby appeals to the United States Court of Appeals for the District of Columbia from the judgment of this Court entered on the 1st day of October, 1940 in favor of Conway P. Coe, Commissioner of Patents, defendant, against said The Dow Chemical Company, plaintiff.

CHRITTON WILES DAVIES HIRSCHL &
DAWSON
2800 Board of Trade Bldg.,
Chigaco, Ill.,
Attorneys for The Dow Chemical
Company, Plaintiff.

NELSON J JEWETT
of counsel

Memorandum

October 19-1940.

Undertaking ($250.00) on appeal of Plaintiff—filed.

80 *Statement of Points Relied on by Plaintiff on Appeal.*

Filed October 28 1940

* * *

Now comes the plaintiff in the above entitled cause, by its counsel, and files the following statement of points relied on by it on appeal from the decree heretofore entered herein dismissing the complaint at plaintiff's costs.

The District Court of the United States for the District of Columbia erred in the following particulars:

1. In refusing to authorize and direct the Commissioner of Patents to issue to plaintiff a patent upon the Britton et al application Serial No. 44,252, filed October 9, 1935.
2. In sustaining and adopting the decision of the tribunals of the Patent Office, holding that the Britton et al invention was not patentable in view of the prior art.
3. In failing to hold that the process of the application, though simple, inexpensive and efficient, did not involve invention.
4. In holding that the patent to Curme, No. 1,518,182, and the patent to Nutting et al, No. 2,007,144, constituted sufficient disclosure to justify the rejection of the Britton et al application.
5. In holding that the Nutting et al patent No. 2,007,144 discloses an operative continuous process for the production of ethylidine chloride.
6. In entering the judgment of October 1, 1940, dismissing the complaint with costs against plaintiff, and in holding that said disclosure was sufficient to justify the rejection of the Britton et al application.

Wherefore, the plaintiff-appellant states that it will rely upon each and all of the errors hereinabove specified, 81 in its appeal to the United States Circuit Court of Appeals for the District of Columbia, and prays that the judgment of this Court entered on October 1, 1940, be reversed, and the costs herein taxed against defendant.

CHRITTON, WILES, DAVIES, HIRSCHL &
DAWSON and NELSON J JEWETT
Counsel for Plaintiff-Appellant.

82 *Designation of Contents of Record on Appeal.*

Filed October 28 1940

* * *

To the Clerk of said Court:

You will please include in the record for appeal to the United States Circuit Court of Appeals for the District of Columbia copies of the following:

1. All pleadings in the case.
2. Transcript of evidence.
3. Memorandum decision of the District Court, dated June 25, 1940.
4. Findings of Fact and Conclusions of Law.
5. Final Judgment dismissing complaint at plaintiff's costs, entered October 1, 1940.
6. Notice of Appeal.
7. Statement of Points relied on by Plaintiff on Appeal.
8. All paper exhibits offered and received in evidence by the parties to the cause.

You will please also certify up to the Court of Appeals as physical exhibits, Plaintiff's Exhibit 6, Reactor, Run No. 7, and Plaintiff's Exhibit 7, Reactor, Run No. 11.

CHRITTON, WILES, DAVIES,
HIRSCHL & DAWSON,
and
NELSON J JEWETT
Counsel for Plaintiff.

Service acknowledged
Oct 25 1940
W. W. COCHRAN
Atty for Defendant

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83 District Court of the United States
for the District of Columbia

UNITED STATES OF AMERICA,
District of Columbia, ss:

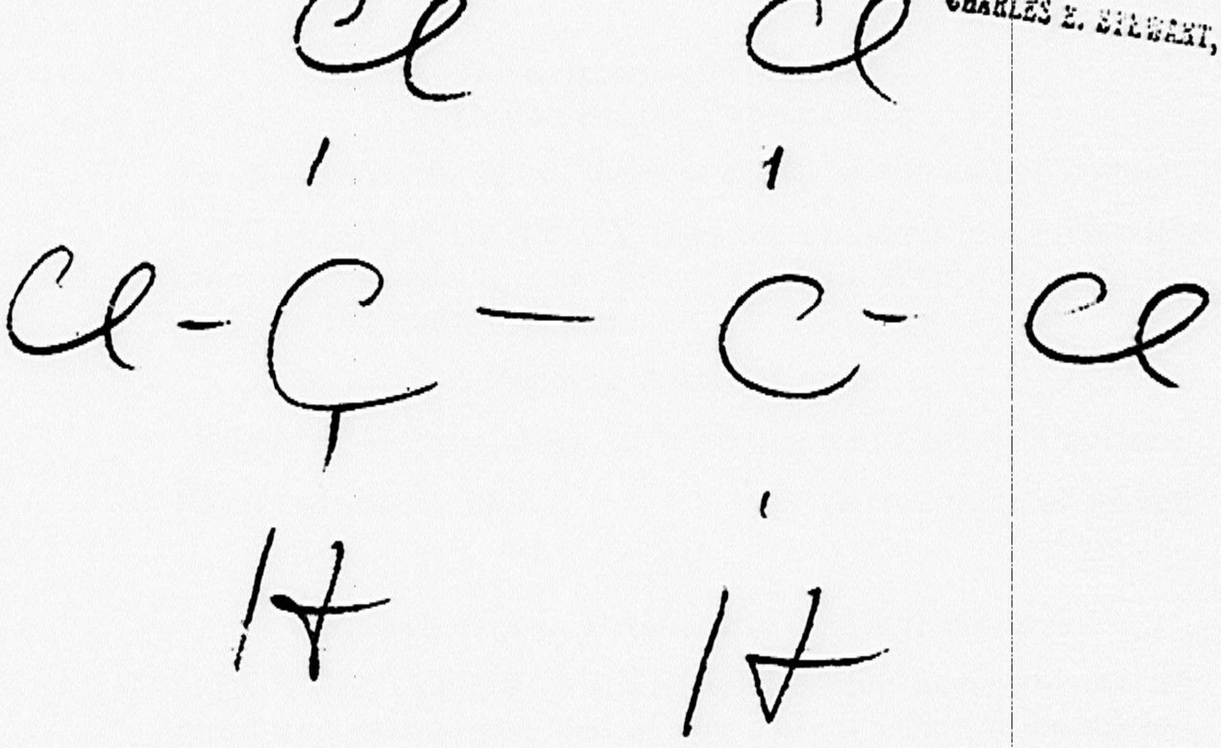
I, Charles E. Stewart, Clerk of the District Court of the United States for the District of Columbia, hereby certify the foregoing pages numbered from 1 to 82, both inclusive, (excepting the transcript of proceedings, as to the accuracy of which counsel has certified), to be a true and correct transcript of the record, according to directions of counsel herein filed, copy of which is made part of this transcript, in cause No. 2924, Civil Action, wherein The Dow Chemical Company is Plaintiff and Conway P. Coe, Commissioner of Patents, is Defendant, as the same remains upon the files and of record in said Court.

IN TESTIMONY WHEREOF, I hereunto subscribe my name and affix the seal of said Court, at the City of Washington, in said District, this 20th day of November, 1940.

C. E. STEWART,
(Seal) *Clerk.*

2124Cd

FILED
OCT 28 1949
CHARLES E. STEWART, Clerk



$$\begin{array}{ccccc} & Cl & & Cl & \\ & | & & | & \\ Cl- & C & - & C & -Cl \\ & | & & | & \\ & H & & H & \end{array}$$

Tetrachloroethane

85 Endorsed: Filed Oct 28 1940 Charles E. Stewart, Clerk

Department of Commerce
United States Patent Office

To all persons to whom these presents shall come, Greeting:

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of the File Wrapper and Contents, in the matter of the

Pending Application of

Edgar C. Britton, Jack L. Williams and Carl F. Prutton,

Filed October 9, 1935, Serial Number 44,252,

for

Improvement in Production of Alkyl Halides.

IN TESTIMONY WHEREOF I have hereunto set my hand and caused the seal of the Patent Office to be affixed, at the City of Washington, this twenty-eighth day of May, in the year of our Lord one thousand nine hundred and forty and of the Independence of the United States of America the one hundred and sixty-fourth.

CONWAY P. COE
(Seal) *Commissioner of Patents.*

Attest:
D. E. WILSON
Chief of Division.

1074

NUMBER (Series of 1935)

44252

PATENT NO.

1935

DATED

BOOK 33

DIV. 6

(EX'R'S BOOK) 26/3

Name EDGAR C. BRITTON, JACK L. WILLIAMS AND CARL F. PRUTTON

Assrs. to The Dow Chemical Company, of Midland, Mich. a corp. of Michigan

of MIDLAND MIDLAND CLEVELAND

State of MICHIGAN OHIO

Invention

PRODUCTION OF ALKYL HALIDES

ORIGINAL		RENEWED
APPLICATION FILED COMPLETE	OCT 9, 1935	
Petition, Specification, Oath, First Fee $30,	OCT 9, 1935	
~~*sheets Drawings,*~~		

Division of App. No. ……, filed ……, 19

Examined and passed for Issue ……, 193	*Reexam'd and passed for Issue* ……, 193
…… *Exr. Div.*	…… *Exr. Div.*
Notice of Allowance ……, 193 *By Commissioner.*	*Notice of Allowance* ……, 193 *By Commissioner.*
Final Fee ……, 193	*Final Fee* ……, 193

Attorney THOMAS GRISWOLD, JR. & E. C. BURDICK C/O THE DOW CHEMICAL CO
MIDLAND MICH

Associate Attorney

No. of Claims Allowed …… *Print Claims* …… *in O.G. Class* ……

Title as allowed

87 Endorsed: Oct—9-35 62899 B—Check—30.00

Endorsed: Mail Division Oct 9 1935 U. S. Patent Office

Endorsed: Paper No. — Oct 15 1935 Division 6

Thomas Griswold, Jr.
E. C. Burdick
Patent Dept.
The Dow Chemical Company
Midland, Michigan

Midland, Michigan, September 16, 1935

Serial No. ....
Filed ....
Inventors Edgar C. Britton, Carl F. Prutton, Jack L. Williams
Patent to be Issued to ....
Title Production of Alkyl Halides

Commissioner of Patents,
Washington, D. C.

Sir:—

In connection with the above entitled case, please apply the enclosed remittance in payment of Patent Office fees in the amounts and for the purpose below indicated:

Patent Application Filing Fee Thirty Dollars ($30.00)
Assignment Record Fee ....
Patent Application Final Fee ....
Appeal to Board of Appeals ....
Appeal to Commissioner ....
....
Remarks:

Respectfully,
THOMAS GRISWOLD, JR.,
E. C. BURDICK,
Attorneys.

88 Endorsed: Mail Division Oct 9 1935 U. S. Patent Office

Endorsed: Paper No. — Oct 15 1935 Division 6

Petition and Power of Attorney

To the Commissioner of Patents:

Your petitioners, Edgar C. Britton and Jack L. Williams, citizens of the United States and residents of Midland, County of Midland, State of Michigan, whose Post Office address is Midland, Michigan, and Carl F. Prutton, a citizen of the United States and a resident of Cleveland, County of Cuyahoga, State of Ohio, and whose Post Office address is Case School of Applied Science, Cleveland, Ohio, pray that Letters Patent may be granted to them for the Improvement in Production of Alkyl Halides set forth in the annexed specification; and they do hereby appoint Thomas Griswold, Jr., (registration No. 12803) and E. C. Burdick (registration No. 13242), of Midland, Michigan, (care of The Dow Chemical Company) either or both, individually or collectively, their attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to receive the patent, and to transact all business connected therewith in the Patent Office.

EDGAR C. BRITTON
JACK L. WILLIAMS
CARL F. PRUTTON

Specification

To All Whom It May Concern:

Be it known that we, Edgar C. Britton and Jack L. Williams, citizens of the United States and residents of Midland, County of Midland, State of Michigan, and Carl F. Prutton, a citizen of the United States and a resident of Cleveland, County of Cuyahoga, State of Ohio, have jointly invented a new and useful Improvement in Production of Alkyl Halides, of which the following is a specification:

The present invention relates to methods for the
89 preparation of alkyl halides by the direct addition of
hydrogen halides to olefines, particularly to methods

for the preparation of alkyl chlorides from olefines and hydrogen chloride; and, more particularly, to methods for the preparation of ethyl chloride by combining ethylene and hydrogen chloride. The term "alkyl halides" as herein used, means alkyl halides which have at least two carbon atoms in the molecule.

The preparation of alkyl chlorides, particularly ethyl chloride, by combining olefines with hydrogen chloride in the presence of catalytic agents such as aluminum chloride, ferric chloride, antimony chloride, etc., under certain conditions, has been described in the patented art, e.g. United States Patents numbers 1 518 182, 1 560 625, 1 637 972, and British Patent 235 521.

We have now invented a continuous process for combining olefines and hydrogen halides to produce alkyl halides, by passing preferably substantially equimolecular proportions of the same through a liquid medium comprising a halogenated aliphatic hydrocarbon compound and an aluminum halide, under anhydrous conditions, at approximately atmospheric pressure, and at temperatures above the boiling point of the alkyl halide produced.

We employ a halogenated aliphatic hydrocarbon, other than the anticipated reaction product, as a suspensory or solvent medium for the aluminum halide catalyst. Such an inert reaction solvent is preferably higher boiling than the anticipated reaction product, is not decomposed by the aluminum halide catalyst at such temperatures as are employed in carrying out the reaction, is not appreciably vaporized at the temperature of reaction, and does not
90 actively take part in the reaction.

The temperature at which the liquid medium is to be maintained is preferably above the boiling point of the alkyl halide to be produced, and is usually between about 12° C. and about 100° C., although somewhat higher temperatures can be used in the preparation of certain alkyl halides. In preparing ethyl chloride we generally conduct our reaction at temperatures ranging between about 12° and about 40° C., because high yields of ethyl chloride are obtained, the ethyl chloride distills from the reaction medium as rapidly as it is formed, and because water can be employed as either the heating or cooling agent within this range of temperature.

Although the combining reaction will take place at slightly super- or sub-atmospheric pressures, we prefer to maintain the reactants and the reactant vessel under approximately atmospheric conditions as regards pressure during the period of reaction. The difficulties inherent to handling large quantities of low boiling and toxic gases under pressure are thus avoided, and high yields of alkyl halide are produced per pound of catalyst because the tendency of the olefine and/ product toward polymerization is materially avoided.

We may employ a pure olefine such as ethylene, propylene, iso-butylene, etc., or mixtures of olefines, in carrying out our invention. We have also used an olefiant gas obtained by the pyrolytic decomposition of petroleum or its fractions. This latter gas may be made, for example, according to the method described in United States Patent number 1 962 502, issued 12 June 1934. The olefines higher than ethylene may be removed by liquifaction and fractional evaporation or by chlorination, leaving a gas where-
of the ethylene content ranges up to 48 per cent by
91 volume, the balance thereof being inert gases such
as hydrogen, methane, ethane, etc.

The following examples illustrate several ways in which our invention may be applied, but are not to be construed as limiting the same.

Example 1

A liquid reaction bath comprising 2000 cubic centimeters of substantially dry tetrachloroethane and 35 grams of anhydrous aluminum chloride was maintained in a vertical glass column at a temperature of about 18° C. An olefiant gas obtained by cracking kerosene, free from olefines higher than ethylene, containing approximately 48.0 per cent by volume of ethylene, the balance being substantially inert gases such as methane, hydrogen, and ethane, was led into the bottom of the reactor. The feed of ethylene was at the rate of 0.73 cubic feet per hour. Simultaneously, dry hydrogen chloride in the amount of 10 per cent excess of the molecular equivalent of anhydrous hydrogen chloride, based on the ethylene, was introduced into the bottom of the reactor. The two gases were passed concurrently into the reaction bath at a substantially uniform rate and at about atmospheric pressure for a period of 60 hours. 40 grams of aluminum chloride was added to the liquid re-

action bath during the time of reaction. The gas leaving the top of the liquid reaction bath was run through a scrubber to remove unreacted hydrogen chloride, dried with anhydrous calcium chloride, absorbed in orthodichlorobenzene, and distilled. A yield of 2486 cubic centimeters of liquid ethyl chloride, measured at —80° C. was obtained. This is an 83.2 per cent yield on the basis of ethylene actually introduced into the liquid bath, and represents a yield
92 of 30.8 pounds of ethyl chloride per pound of aluminum chloride catalyst used.

Example 2

A vertical glass column containing 225 cubic centimeters of dry tetrachloroethylene and 40 grams of anhydrous aluminum chloride was maintained at a temperature of 25° C. for 72 hours, during which time an average of 0.45 cubic feet per hour of pure ethylene gas, and dry hydrogen chloride gas in slight excess of theoretical based on the ethylene, were concurrently bubbled through the bath at a substantially uniform rate and at atmospheric pressure. After 45 hours, an additional 125 cubic centimeters of tetrachloroethylene and 15 grams of aluminum chloride catalyst were added to the reaction bath. The gas leaving the top of the reactor was collected and purified, as described in Example 1. A yield of 2370 cubic centimeters of liquid ethyl chloride, measured at —70° C., representing 97 per cent of theoretical yield was obtained. This is a yield of 44 pounds of ethyl chloride per pound of aluminum chloride used. Substantially no tar formation due to side reactions involving polymerization was observed in this reaction.

Example 3

A vertical glass column containing a mixture of 225 cubic centimeters of dry tetrachloroethylene and 45 grams of anhydrous aluminum chloride was held at 40° C. for 68 hours. During this period an average of 0.45 cubic feet per hour of 100 per cent ethylene gas and a slight molecular excess of anhydrous hydrogen chloride gas was passed concurrently through the reaction bath. A yield of 1763 cubic centimeters of pure liquid ethyl chloride, meas-
93 ured at —80° C., was obtained from the gas evolved from the reactor. This is a 77 per cent of theoretical yield, on the basis of ethylene passed through the reactor,

and represents a yield of 36 pounds of ethyl chloride per pound of aluminum chloride used.

We have carried out our process for the production of alkyl chlorides such as propyl and butyl chlorides and particularly ethyl chloride, in reaction media comprising aluminum chloride contained in symmetrical dichloroethane, symmetrical dichloropropane, 1·1·2-trichloroethane, pentachloroethane, and mixtures of two or more of the same. We can readily prepare alkyl bromides such as ethyl, propyl, and butyl bromides, by combining olefines and hydrogen bromide in reaction media comprising aluminum bromide and a liquid brominated aliphatic hydrocarbon such as symmetrical dibromopropane, symmetrical dibromoethane, etc. Chloro-bromo-compounds, as well as mixtures of chloro- and bromo-aliphatic hydrocarbons also constitute suitable reaction media. In any event, the reaction medium must be liquid under the temperature conditions employed in carrying out the combining reaction between the olefine and hydrogen halide. Yields of alkyl halide obtained during the carrying out of the foregoing experiments varied between 75 per cent and 95 per cent of theoretical.

By carrying out the combining reaction between olefines and hydrogen halides in a liquid halogenated aliphatic hydrocarbon, in the presence of an aluminum halide, local overheating of the reacting gases is avoided, thereby reducing the tendency of the olefine to polymerize. Under the temperature conditions we employ, the alkyl halide is distilled from the reaction medium as rapidly as it is
formed, which avoids polymerization of the product
94 through prolonged contact with the reaction catalyst.

The carrying out of the invention at substantially atmospheric pressures avoids the difficulty which is encountered in handling gaseous reactants under the relatively high pressures employed in the prior art. The absence of an appreciable amount of polymerized material in the reaction mixture avoids rapid poisoning of the aluminum halide catalyst, thereby increasing the amount of alkyl
halide obtainable from a given amount of catalyst.

95 Other modes of applying the principle of our in-
vention may be employed instead of those explained, change being made as regards the method herein disclosed,

provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:

—1—

In a process for the production of alkyl halides, the step which consists in passing an olefine and a hydrogen halide, under substantially anhydrous conditions, into a reaction bath comprising a halogenated aliphatic hyrocarbon and an aluminum halide, while the bath is maintained at a temperature above the boiling point of the alkyl halide to be produced and under approximately atmospheric pressure.

—2—

In a process for the production of alkyl chlorides, the step which consists in passing an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising a halogenated aliphatic hydrocarbon and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

—3—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of a chlorinated lower aliphatic hydrocarbon and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—4—

96 In a process for the production of alkyl chlorides, the step which consists in passing an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising a chloroethane derivative and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

—5—

In a process for the production of alkyl chlorides, the step which consists in passing an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising a chloroethylene derivative and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

—6—

In a process for the production of alkyl chlorides, the step which consists in passing an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising tetrachloroethane and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

97 —7—

In a process for the production of alkyl chlorides, the step which consists in passing an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising tetrachloroethylene and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

—8—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of a chloroethane derivative other than the product of the reaction, and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—9—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of a chloroethylene derivative and aluminum chloride, while the bath is maintained at a temperature between 12° C. and 40° C. and under approximately atmospheric pressure.

98 —10—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethane and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—11—

In a process for the production of alkyl halides, the step which consists in passing, in substantially equimolecular proportions, an olefine and a hydrogen halide, under substantially anhydrous conditions, into a reaction bath comprising a halogenated aliphatic hydrocarbon and an aluminum halide, while the bath is maintained at a temperature above the boiling point of the alkyl halide to be produced and under approximately atmospheric pressure.

—12—

In a process for the production of alkyl chlorides, the step which consists in passing, in substantially equimolecular proportions, an olefine and hydrogen chloride, under substantially anhydrous conditions, into a reaction bath comprising a chlorinated aliphatic hydrocarbon and aluminum chloride, while the bath is maintained at a temperature above the boiling point of the alkyl chloride to be produced and under approximately atmospheric pressure.

99 —13—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of a chlorinated lower aliphatic hydrocarbon and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—14—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethane and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—15—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethylene and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

[Matter enclosed between rules erased in copy.]

Signed by us this 4 day of October, 1935.

EDGAR C. BRITTON
JACK L. WILLIAMS

Signed by me this 27 day of September, 1935.

CARL F. PRUTTON

100 *Oath*

STATE OF OHIO
County of Cuyahoga, ss:

Carl F. Prutton, being duly sworn, deposes and says that he is a joint applicant with Edgar C. Britton and Jack L. Williams for the invention described and claimed in the foregoing specification, a citizen of the United States and a resident of Cleveland, Ohio; that he does verily believe that they are the original, first, and joint inventors of the Improvement in Production of Alkyl Halides, described and claimed in the foregoing specification, signed by them; that he does not know and does not believe that the same was ever known or used before their invention or discovery thereof; or patented or described in any printed publication in this or any foreign country before their invention or discovery thereof, or more than two years prior to this application, or in public use or on sale in this country for more than two years prior to this application; that their invention has not been patented to themselves or others with his knowledge or consent in any foreign country on an application filed by them, or their legal representatives or assigns, more than twelve months prior to this application; and that no application for patent on same has been filed by them, or their legal representatives or assigns in any foreign country.

CARL F. PRUTTON

Sworn to and subscribed before me this 27 day of September, 1935.

ELVA R. WEST
(Seal) *Notary Public.*

My Commission Expires Oct. 21, 1936

101 *Oath*

STATE OF MICHIGAN,
County of Midland, ss:

Edgar C. Britton and Jack L. Williams, being duly sworn, depose and say that they are joint applicants with Carl F. Prutton for the invention described and claimed in the foregoing specification, citizens of the United States and residents of Midland, Michigan; that they do verily believe that they are the original, first and joint inventors of the Improvement in Production of Alkyl Halides, described and claimed in the foregoing specification, signed by them; that they do not know and do not believe that the same was ever known or used before their invention or discovery thereof, or patented or described in any printed publication in this or any foreign country before their invention or discovery thereof, or more than two years prior to this application, or in public use or on sale in this country for more than two years prior to this application; that their invention has not been patented to themselves or others with their knowledge or consent in any foreign country on an application filed by them, or their legal representatives or assigns, more than twelve months prior to this application; and that no application for patent on same has been filed by them, or their legal representatives or assigns in any foreign country.

EDGAR C. BRITTON
JACK L. WILLIAMS

Sworn to and subscribed before me this 4th day of October, 1935.

GENEVA TURNER
(Seal) *Notary Public*
My Commission expires July 8, 1938.

102 Div. 6 Room 4898C CAC/ah Paper No. 2
Mailed Jan 10 1936

Department of Commerce
United States Patent Office
Washington

Please find below a communication from the Examiner in charge of this application.

CONWAY P. COE,
Commissioner of Patents,

Applicant: E. C. Britton et al
Ser. No. 44252
Filed Oct. 9, 1935
For Production of Alkyl Halides

Thomas Griswold, Jr.
& E. C. Burdick
c/o The Dow Chemical Co.
Midland, Mich.

Examined.
References made of record:

Curme	1,545,742	July 14, 1925	260-166
Nutting et al	2,007,144	July 2, 1935	260-162

In the petition, the post office address of Carl F. Prutton should be completed by adding the city and state.

Claims 1 to 15 are rejected as being unpatentable over Curme alone or especially in view of Nutting et al. In line 46 Curme states that the solvent employed may be the reaction product or any anhydrous solvent. No particular result is obtained by using the solvents in the claims which are

related chemically to those suggested in Curme. Only the obvious, expected result is obtained by using the temperature specified in the claims. The claims at present are broad enough to include the reaction of the olefine and hydrogen chloride in a vapor phase diluted by the vapor of the product, which is precisely what occurs in the reaction of Curme as specified in lines 42 to 44. Nutting et al suggest the use of numerous solvents including some of those claimed, and,
in lines 8 to 10 on page 2, provides for the distillation
103 of the product as it is formed. It is thought that no
invention would be required to substitute the reaction media disclosed in lines 50 to 55 on page 1 of Nutting et al for those of Curme, since only obvious, expected results would be obtained by such substitution.

Claims 1, 2, 4 to 7, 11, 12 and 13 are further rejected as failing to define the invention and as being broader than the invention. Any and all alkyl halides in the bath will not operate as desired with any and all olefines. Obviously, if a long-chain olefine were reacted in such general and specific alkyl halide baths as claimed, the results desired would not be obtained.

Claims 1 to 15 are further rejected as failing to define the invention and as being broader than the invention in that they would include temperatures above the boiling point of the reaction bath at the pressure disclosed. From the disclosure, this appears to be beyond the scope of the invention.

Claims 1 and 11 are rejected as being broader than the invention. In claim 1, "hydrogen halide", and in claim 11, "aluminum halide" are broader than the invention in that there is no evidence that any and all such halides will be operative. Obviously, HF will not react under the conditions stated.

A. M. LEWERS,
Examiner.

C.A.C.

104 Mail Division Jun 19 1936 U. S. Patent Office
Paper No. 3 Jun 19 1936 Division 6

Midland, Michigan, June 13, 1936

Applicants E. C. Britton et al.
Serial No. 44,252
Filed October 9, 1935
For "Production of Alkyl Halides"

Div. 6, Room 4898C

Hon. Commissioner of Patents

Sir:

In response to Office action dated January 10, 1936, I hereby amend as follows:—

In the Petition, lines 8 and 9, following "Case School of Applied Science", insert—Cleveland, Ohio,—.

Page 7, following the final paragraph, insert the following:—

—The terms "ethyl halide", "hydrogen halide", and "aluminum halide" as used in the specification and claims of this application refer to ethyl chloride and ethyl bromide, hydrogen chloride and hydrogen bromide, and aluminum chloride and aluminum bromide, respectively—.

Cancel claims 1, 2, 4, 5, 6, 7, 11, and 12.

Claim 3, line 3, following "into a" insert—liquid—; line 4, following "chlorinated" insert—lower—; lines 5 and 6, cancel "above the boiling point of ethyl chloride" and substitute therefor—between 12° C. and the boiling temperature thereof—.

Claim 8, line 3, following "into a" insert—liquid—; lines 6 and 7, cancel "above the boiling point of ethyl chloride" and substitute therefor—between 12° C. and the boiling temperature thereof—.

Claim 9, line 3, following "into a" insert —liquid—; lines 5 and 6, cancel "above the boiling point of ethyl chloride" and substitute therefor —between 12° and 40° C.—

105 Claim 10, line 3, following "into a" insert —liquid—; lines 5 and 6, cancel "above the boiling point of ethyl chloride" and substitute therefor —between 12° C. and the boiling temperature thereof—.

Claim 13, line 4, following "into a" insert —liquid—; line 5, following "chlorinated" insert —lower—; lines 6 and 7, cancel "above the boiling point of ethyl chloride" and substitute thereof —between 12° C. and the boiling temperature thereof—.

Claim 14, line 4, following "into a" insert —liquid—; line 6, cancel "above the boiling point of ethyl chloride" and substitute therefor —between 12° C. and the boiling temperature thereof—.

Claim 15, line 4, following "into a" insert —liquid—; lines 6 and 7, cancel "above the boiling point of ethyl chloride" and substitute therefor —between 12° C. and the boiling temperature thereof—.

Please add the following new claims:—

—16—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath comprising a halogenated lower aliphatic hydrocarbons, and aluminum chloride, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—17—

In a process for the production of ethyl chloride, the steps
which consist in passing ethylene and hydrogen chloride,
under substantially anhydrous conditions into a liquid reac-
tion bath comprising a halogenated lower aliphatic
106 hydrocarbons, and aluminum chloride, while the bath
is maintained at a temperature between 12° C. and
the boiling temperature thereof, and under approximately
atmospheric pressure, and continuously distilling off ethyl
chloride product substantially as formed.

—18—

In a process for the production of an ethyl halide, the step which consists in passing ethylene and a hydrogen halide, under substantially anhydrous conditions, into a liquid reaction bath comprising a halogenated lower aliphatic hydrocarbons, and aluminum halide, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof and under approximately atmospheric pressure.

—19—

In a process for the production of ethyl halide, the steps which consist in passing ethylene and a hydrogen halide, under substantially anhydrous conditions into a liquid reaction bath comprising a halogenated lower aliphatic hydrocarbons, and aluminum halide, while the bath is maintained at a temperature between 12° C. and the boiling temperature thereof, and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

—20—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions into a liquid reaction bath comprising a halogenated lower aliphatic hydrocarbons, and aluminum chloride, while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

—21—

107 In a process for the production of ethyl halide, the steps which consist in passing ethylene and hydrogen halide, under substantially anhydrous conditions into a liquid reaction bath comprising a halogenated lower aliphatic hydrocarbon and aluminum halide, while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

[Matter enclosed between rules erased in copy.]

Remarks

The Petition has been completed as requested by Examiner.

All claims reading broadly to the preparation of alkyl halides have been cancelled, and the remaining claims amended to limit them to the essentially novel features of the invention. New claims 16 to 21, inclusive, which are believed to define patentable subject matter, have been added.

The disclosure of the Curme reference is limited to a process by which isopropyl chloride may be prepared, and contains no mention of ethylene or ethyl chloride. Curme teaches that propylene and hydrogen chloride may be reacted to form isopropyl chloride by bringing them into contact in an anhydrous, gaseous condition. The yield is said to be increased by subjecting the reacting gases to pressures above normal, e.g. 15 atmospheres, with or without increased temperatures. Data as regards proportions of reactants, yields, temperatures of reaction, etc., are completely lacking in the description. Obviously, Curme does not teach a complete and operable method for the preparation of alkyl halides generally. Curme's remarks as regards the general use of solvents are entirely prophetic and the only solvent specifically suggested is the
108 product of reaction. The expression "or other suitable solvent" found on line 46 of the reference gives no instruction to workers in the art, and cannot be interpreted in the light of subsequent findings to include all possible reaction media, since Curme has offered no examples to indicate that he had any conception of what would or would not constitute suitable media.

It is well established in the art that ethylene is much less reactive than its homologues, e.g. propylene, and in a great many processes designed for the preparation of derivatives and polymers of olefinic materials any ethylene present in the olefinic mixture is recovered as an unreacted residue. This difference in reactivity has been frequently utilized as a method for the separation of an olefinic mixture into its constituents. For example, see U. S. Patents Nos. 1,822,358; 1,872,080; etc. Furthermore, many known processes for the preparation of the alkyl chlorides by the reaction of olefines with HCl have been found not to be applicable to the preparation of ethyl chloride as illustrated in British Patent No. 414,766 (dated February 12, 1934), lines 95-100; and British Patent No. 235,547 (dated May 26, 1925), lines 40-45. The above British applications teach that contacting ethylene and hydrogen chloride, under anhydrous conditions, even in the presence of catalysts suitable for the condensation of hydrogen chloride with ethylene homologues, does not cause these two gases to react to form the desired halide. It is apparent from their teaching that ethylene would not react with hydrogen chloride gas in a manner similar to propylene in the preferred process of Curme and an experimenter attempting to adapt Curme's isoproyl chloride process to a method for preparing ethyl chloride would be led away from, rather than toward, the desired end.

Curme teaches no temperatures for reaction but states merely that heating may be employed if desired. The citation of Curme against this application can only be on
109 the grounds that Curme suggests the use of the reaction product as a solvent for reaction, and it is pointed out that the reaction product of applicants' process is not included within the scope of the claims since at the temperatures to which each claim is limited, applicants' reaction product would be gaseous in nature and thereby fail to qualify as a liquid reaction bath. As pointed out by Examiner, Curme's reaction is particularly concerned with the reaction of the olefine and hydrogen chloride in the vapor phase diluted by the vapor of the product. All of the claims of this application are limited to reactions involving a liquid reaction bath and are believed to be patentably distinct over Curme.

The disclosure of Nutting et al. is limited specifically to the description of various methods for the preparation of ethylidene chloride by the reaction of hydrogen chloride with vinyl chloride in the presence of a suitable catalyst. No mention is made in this reference as to the equivalency of any olefine with the vinyl chloride in the process, and it is not seen how a process adapted to be carried out on a halogen derivative such as vinyl chloride can be construed to anticipate or suggest the invention here claimed. The product ethylidene chloride, and the problem of making the same from vinyl chloride, have nothing in common with the products and problems of applicants. Here, as in Curme, the teaching of the preferred embodiment is to utilize one of the reactants or the product of reaction as reaction media, which is obviously outside the scope of applicants' claims and impossible of achievement under the conditions outlined by applicants' disclosure.

Examiner has stated that only the obvious, expected result is obtained by using the temperatures specified in the claims. It may be pointed out that these temperatures, namely, 12° C. to the boiling point of the reaction bath, have been determined as a result of extensive experimentation on the part of applicants and have been found
110 to be of vital importance in the successful preparation of ethyl chloride by the described process. The lower limit of 12° C. represents the lowest temperature at which the ethyl chloride may be distilled from the reaction mixture substantially as formed. Such removal of the product from the reaction zone prevents the polymerization and further decomposition of the same due to unnecessarily prolonged contact with the aluminum halide catalyst. Such decomposition constitutes a major disadvantage in many of the alkyl halide processes at present known to the art. It also prevents the inactivation of suspended catalyst particles in the bath due to formation of gummy films of polymerized material upon the surface of such particles and increases the yield of product per pound of catalyst employed. The upper limit, namely, the boiling point of the bath, eliminates the distillation of contaminating reaction solvent along with the reaction product and thereby obviates the additional step of purification of the ethyl halide. The temperature limits called for in the claims are not disclosed or suggested by the references of record and no reason is seen for considering their choice obvious.

In rejecting the present invention on Curme in view of Nutting et al., Examiner has apparently overlooked the well established policy of the Office to the effect that for a combination of references to anticipate properly an application, at least one of the references should ordinarily show the general invention or subject matter claimed. It has been shown that neither of the references describes or suggests applicants' invention and it is, therefore, respectfully requested that Examiner's objections on the basis of the references of record be withdrawn.

Claims 3, 8, 9, 10, and 13 to 15, inclusive, rejected by the Examiner as failing to define the invention and as being broader than the invention have been amended and
111 now read specifically to liquid reaction baths com-

prising halogenated lower aliphatic hydrocarbons and to temperatures of reaction which eliminate the possibility that such claims might be construed to cover the reaction of ethylene with hydrogen halide in the gaseous phase.

New claims 16 to 21, inclusive, have been drawn narrowly to a process for the preparation of ethyl halide and ethyl chloride, and are limited to the "liquid reaction bath comprising a halogenated lower aliphatic hydrocarbon" feature and to the particular temperatures found most suitable. They are believed to be patentably distinct from the references of record.

The specification has been amended to include a definition of the terms "ethylene halide", "hydrogen halide", and "aluminum halide", previously objected to as being broader than the invention by the Examiner.

Applicants' invention is in no way disclosed by the references cited, and since the claims are now all limited to the essentially novel features of the reaction bath and temperature, it is believed that they define patentable subject matter and allowance of this application is accordingly solicited.

Respectfully,
THOMAS GRISWOLD, JR.,
Attorney.

BLF:GT

112 Endorsed: Mailed Sep-3 1936

Div. 6 Room 4898C B/ah Paper No. 4

Department of Commerce
United States Patent Office
Washington

Applicant: E. C. Britton et al
Ser. No. 44,252
Filed Oct. 9, 1935
For Production of Alkyl Halides

Thomas Griswold, Jr. & E. C. Burdick
c/o The Dow Chemical Co.
Midland, Mich.

Responsive to amendment filed June 19, 1936.

Claims, 3, 8, 9, 10, 13, 14 and 15 are rejected as being too broad in "comprising". This would include the use of other substances in the bath besides those disclosed. An exclusive term, such as *—consisting of—*, should be used. No other ingredient in the bath other than the lower alkyl chloride is disclosed.

Claims 18, 19 and 21 are rejected as being too broad in "halide". Only the chlorine and bromine compounds have been disclosed. This term has a well known meaning in the art which cannot be changed to suit the applicants, as is attempted in the amendment of June 19, 1936.

Claims 16 to 21 are rejected as being too broad in "halogenated . . . hydrocarbon". Only lower chlorinated hydrocarbons have been disclosed and others cannot be presumed to be operative.

O. F. STEARNS
Acting Examiner.

113 Endorsed: Docket Division Feb 26 1937 U. S. Patent Office

Endorsed: Paper No. 5 Feb 26 1937 Division 6

Endorsed: Mail Division Feb 25 1937 U. S. Patent Office

In the United States Patent Office

Applicants E. C. Britton et al.
Serial No. 44 252
Filed 9 October 1935
For "Production of Alkyl Halides"

Substitute Power of Attorney

Div. 6, Room 4898C
Hon. Commissioner of Patents
Sir:

We hereby appoint GRISWOLD & BURDICK, a firm composed of Thomas Griswold, Jr., E. C. Burdick, H. A. Stearns, J. W. Rebbeck, Dean Laurence, and Bruce L. Fayerweather, Registration No. 14262, whose Post Office address is, care of The Dow Chemical Company, Midland, Michigan, substitute attorneys in the matter of the above entitled application, with full power in the premises.

Respectfully
THOS. GRISWOLD Jr.

Midland, Michigan
23 February 1937

114 Endorsed: Docket Division Feb 26 1937 U. S. Patent Office

Endorsed: Paper No. 6 Feb 26 1937 Division 6

Endorsed: Mail Division Feb 25 1937 U. S. Patent Office

Division 6 Room 4898C Paper Number

Midland, Michigan, 23 February 1937

Applicants: E. C. Britton et al.
Serial Number: 44 252
Filed: 9 October 1935
For: "Production of Alkyl Halides"

The Commissioner of Patents
Washington, D. C.

Sir:

In response to Office action dated 3 September 1936, we hereby amend as follows:

Claims 3, 8, 9, 10, 13, 14, and 15, line 4 of each, cancel "comprising" and insert—consisting substantially of—.

Claims 18, 19, and 21, line 1 of each, after "halide" insert—selected from the group consisting of ethyl chloride and ethyl bromide—. Same claims, line 2 of each, after "halide" insert —selected from the group consisting of hydrogen chloride and hydrogen bromide—.

[Matter enclosed between rules erased in copy.]

Remarks

Claims 3, 8, 9, 10, 13, 14, and 15, objected to as too broad in "comprising" have been amended by substituting therefor the term "consisting substantially of". It is thought that the applicants should not be limited to a bath wherefrom all ingredients other than lower alkyl halides be excluded because if such is done a user might attempt to appropriate the substance of applicants' invention by adding a small amount of an inert material. The claims are, therefore, directed to the use of baths which consist substantially of lower alkyl halides but are so worded as 115 not to exclude the presence of inert diluents which would have no effect upon the course of the hydrohalogenation reaction. It is noted that on page 6 of applicants' specification liquid brominated aliphatic hydrocarbons and chloro-bromo- compounds, as well as mixtures of chloro- and bromo-aliphatic hydrocarbons, are stated to constitute suitable reaction media.

Claims 18, 19, and 21 objected to as being too broad in "halide" have been amended by the use of a Markush expression to limit these claims to the chloro- and bromo-compounds.

Claims 16 to 21 have been objected to as being too broad in "halogenated .... hydrocarbon" with the statement that "Only lower chlorinated hydrocarbons have been disclosed ...." As above pointed out, bromo- compounds, chloro-bromo- compounds and mixtures of chloro- and bromo- lower aliphatic hydrocarbons, have been disclosed on page 6 of applicants' specification as constituting suitable reaction media. It is, therefore, not believed necessary to change the expression to which objection has been made in said claims. If the Examiner prefers, a Markush expression directed to the particular materials disclosed will be substituted for the term to which objection has been made.

It is believed that this application is in condition for final allowance and action to that end is accordingly solicited.

Respectfully
GRISWOLD & BURDICK
Attorneys

DRL:IS

116 Endorsed: Mailed Jun 12 1937

Div. 6 Room 4898C WT/ah Paper No. 7

Department of Commerce
United States Patent Office
Washington

Applicant: E. C. Britton et al
Ser. No. 44,252
Filed Oct. 9, 1935
For Production of Alkyl Halides

Griswold & Burdick
c/o The Dow Chemical Co.
Midland, Mich.

Responsive to amendment filed Feb. 25, 1937.

Claims 16 to 21 are each rejected as being broader than the invention in "comprising". Reference to these claims was inadvertently omitted in the last Office action. See the rejection of claims 3, 8, 9, 10, 13, 14 and 15 in the previous Office action.

Claims 16 to 21 are each again rejected as being broader than the invention in "halogenated . . . hydrocarbon. Applicants have disclosed only chlorinated and brominated hydrocarbons, and the claims should be so limited.

Claims 3, 8, 9, 10, 13, 14 and 15 are allowable so far as now known.

A M LEWERS
W.T. *Examiner.*

117 Endorsed: Paper No. 8 Aug 13 1937 Division 6

Endorsed: Mail Division Aug 13 1937 U. S. Patent Office

Midland, Michigan, 1937 August 10

Applicants E. C. Britton et al.
Serial No. 44 252
Filed 1935 October 9
For "Production of Alkyl Halides"

Div. 6, Room 4898C
Hon. Commissioner of Patents

Sir:

In response to Office action of 1937 June 12, we hereby amend as follows:

Claims 16 to 21, line 4 of each, cancel "comprising a halogenated" and substitute therefor —consisting substantially of a material selected from the group consisting of the chlorinated and brominated—. Same line, pluralize "hydrocarbon", and insert a comma thereafter.

[Matter enclosed between rules erased in copy.]

Remarks

This application appears to be in condition for final allowance, to which end action is accordingly solicited.

Respectfully,

GRISWOLD & BURDICK
DRL:kh *Attorneys*

118 Endorsed: Mailed Nov 3 1937

Div. 6 Room 4898C T:hw Paper No. 9

Department of Commerce
United States Patent Office
Washington

Applicant: E. C. Britton et al
Ser. No. 44,252
Filed Oct. 9, 1935
For Production of Alkyl Halides

Griswold & Burdick
c/o The Dow Chemical Co.
Midland, Mich.

Responsive to amendment filed August 13, 1937.
The following reference is added to the record:

Curme 1,518,182 Dec. 9, 1924 260-166

In view of the newly cited reference to Curme, the allowance of claims 3, 8, 9, 10, 13, 14, and 15 is withdrawn. Claims 3, 8, 9, 10, and 13 to 21 are each rejected as being unpatentable over Nutting #2,007,144, in view of Curme #1,518,182. Nutting discloses a process of making ethylidene chloride by passing a gaseous mixture of vinyl chloride and hydrogen chloride into a bath consisting of aluminum chloride suspended in an organic solvent such as trichlorethane or tetrachlorethane. It is evident that Nutting operates his process at such a temperature and pressure that the ethylidene chloride produced in the reaction exists in the vapor phase, (Nutting, page 1, col. 2, line 52 to page 2, col. 1, line 17) and thus the process is carried out continuously, the vinyl chloride and hydrogen chloride being continuously passed into the catalytic bath and the product being continuously withdrawn. The examiner is of the belief that it would be an obvious expedient to substitute ethylene for the vinyl chloride of Nutting in view of Curme. Vinyl chloride is derived from ethylene by the replacement of one hydrogen atom with chlorine, i.e., $CH=CHCl$. It is to be noted that vinyl chloride still contains a double bond, and a person skilled in the art would readily recognize that ethylene would react with hydrogen chloride in a

119 manner similar to vinyl chloride. Curme, #1,518,182,
discloses a process of making ethyl chloride by reacting ethylene and hydrogen chloride in the presence of aluminum chloride as a catalyst. The examiner is of the opinion that it would be an obvious extension of the teaching of Nutting to substitute ethylene for the vinyl chloride (monchlorethylene) as used by Nutting, in view of Curme.

Claims 3, 9, 13, and 16 to 21 are each rejected as being broader than the invention in that these claims do not specifically exclude the use of ethyl chloride as the reaction medium. It does not appear that applicants have contemplated the use of ethyl chloride. This defect may be remedied by stating the use of a chlorinated lower aliphatic hydrocarbon which has a boiling point above that of ethyl chloride.

Claim 8 is rejected on the same grounds as claims 3, 9, 13, and 16 to 21, above. It is noted that in this claim applicants state: "a chlorethane derivative other than the product of the reaction." It is not believed that this limitation is sufficient. It appears that applicant has disclosed the use of only chlorethane derivatives which have boiling points higher than that of ethyl chloride and the claims should be so limited.

Claims 3, 8, 10, and 13 to 19 are each rejected as being indefinite and broader than the invention. These claims recite a "liquid reaction bath" and then go on to say that the "bath is maintained at a temperature between 12° C. and the boiling temperature thereof." It is evident that if the temperature is maintained at the boiling temperature, the
bath cannot be maintained in the liquid state. This
120 defect can be corrected if it were specified that the
bath is maintained at a temperature above 12°C. but below the boiling temperature of the bath.

Claims 9, 20, and 21 are each rejected on the same grounds as claims 3, 8, 10, and 13 to 19, above. It is to be noted that the specifying of 40° as the upper limit of the temperature range is not sufficient as the claims would include a solvent which boils at less than 40°.

A M LEWERS
W.T. *Examiner*

121 Endorsed: Paper No. 10 Apr 2 1938 Division 6

Endorsed: Mail Division Apr 1 1938 U. S. Patent Office

Midland, Michigan, March 30, 1938

Applicants E. C. Britton et al.
Serial No. 44,252
Filed October 9, 1935
For "Production of Alkyl Halides"

Div. 6, Room 4898C
Hon. Commissioner of Patents

Sir:

In response to Office action of November 3, 1937, we hereby amend as follows:

Cancel claims 3, 8-10, and 13-21, inclusive, and substitute therefor the following new claims:

—22—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—23—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum 122 chloride and a chloroethane derivative having a boiling point higher than that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—24—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chloroethylene derivative having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C. and under approximately atmospheric pressure.

—25—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—26—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction 123 bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—27—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—28—

In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethylene and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—29—

In a process for the production of ethyl chloride, the step
which consists in passing ethylene and hydrogen chloride,
under substantially anhydrous conditions, into a
124 liquid reaction bath consisting substantially of alumi-
num chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—30—

In a process for the production of ethyl chloride, the steps which consist in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

—31—

In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the step which consists in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic
liquid selected from the group consisting of those
125 chlorinated and brominated lower aliphatic hydro-
carbons having a boiling point above that of ethyl

chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

—32—

In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

—33—

In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

—34—

126 In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons

having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

Remarks

Curme, U. S. Patent No. 1,518,182, describes a vapor phase reaction of ethylene with anhydrous hydrogen chloride in the presence of aluminum chloride and preferably under super-atmospheric pressure. Curme does not teach the use of any solvent as a reaction bath or in any way suggest the invention defined by rewritten claims 22-34.

Nutting has been discussed at length in previous responses and been clearly shown not to anticipate the present invention. The combination of Curme with Nutting is both unjustified and ineffectual. There is no suggestion in either of these references or in the art to combine the references, nor does either reference teach applicants' invention as is generally considered essential for such 127 a combination of references to be proper. There is no such similarity between vinyl chloride and ethylene as would suggest to one skilled in the art that these compounds are interchangeable in the process disclosed by either of the references. Nutting points out on page 1, lines 5 through 28, that vinyl chloride is in no sense the equivalent of ethylene, and that vinyl chloride cannot be successfully combined with hydrogen chloride by a method substantially identical with that disclosed by Curme. If, as contended by Examiner, vinyl chloride and ethylene are equivalents, a person skilled in the art would expect that vinyl chloride could be reacted in a manner analogous to ethylene to form the corresponding hydro-halogenated derivative, e. g. as in the Curme reference. That such is not the case positively refutes Examiner's claim of equivalency for the two compounds. The fact that applicants have discovered a process in which vinyl chloride and ethylene may possibly be equivalents does not warrant the interpretation of the prior art in the light of that discovery by the Examiner. The combination of the references is clearly improper.

Even when the references are combined, a careful study of Nutting discloses that the combination fails to teach or appreciate the invention claimed by applicants. The statement by Examiner that "Nutting operates his process at such a temperature and pressure that the ethylidene chloride produced in the reaction exists in the vapor phase'' is not supported by the disclosure of the Nutting patent. In fact, Nutting discloses the retention of the ethylidene chloride product in the reaction zone as a reaction bath into which additional vinyl chloride and hydrogen chloride are preferably passed to accomplish the desired reaction. On page 1, lines 37 through 40, Nutting points out that

128 ''During the reaction, the liquid vinyl chloride, which is employed both as a reactant and as the reaction medium, is converted to ethylidene chloride, which in turn serves as the liquid reaction medium.''

Certainly this teaching is not to the end that the product of reaction, or for that matter the reactant vinyl chloride, exists in the vapor phase at any time during the reaction. Each of Nutting's Examples illustrates an experiment in which the product of reaction, i.e. ethylidene chloride, is held within the reaction mixture until the completion of the process subsequently being recovered as by distillation. The question may reasonably be asked in consideration of Examiner's contention as to the equivalency of ethylene and ethyl chloride with vinyl chloride and ethylidene chloride, respectively: Could ethylene and ethyl chloride be employed as reaction media in the process and at the temperatures and pressures defined in each of applicants' claims? The answer is ''no''.

With respect to the teaching of Nutting on page 1, column 2, line 52 to page 2, column 1, line 17, it is believed that the Examiner has misinterpreted the patentee's disclosure. On page 2, column 1, lines 4 through 10, Nutting teaches as follows

''A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed.''

If we are to assume that Nutting actually contemplated the continuous distillation of his ethylidene chloride product from the reaction mixture as disclosed in the foregoing quotation, we are faced with the proposition that in

129 continuously distilling the reaction product from the mixture he would also distill out of the reaction zone the ethylidene chloride employed as reaction medium, the presence of which is essential to the carrying out of his process. It is clear from the foregoing that any prophetic remarks made by Nutting as to the practicability of continuously distilling ethylidene chloride from a reaction mixture comprising that compound as reaction medium would defeat the very purpose of his invention. Such teaching is not considered ample basis to support the present rejection, particularly in view of the fact that Example 1, which evidently constitutes an effort on the part of Nutting to illustrate the continuous preparation of ethylidene chloride, clearly discloses a reaction temperature below the boiling point of ethylidene chloride and teaches that the ethylidene product is recovered by steam distillation of the reacted mixture. In light of the foregoing, it is evident that a combination of Nutting and Curme does not anticipate applicants' invention.

Claims 3, 8-10, and 13-21 have been rewritten as claims 22-34, which are believed to be in proper form and to define subject matter patentable over the references of record. Reconsideration and final allowance are solicited.

Respectfully,
GRISWOLD & BURDICK
Attorneys

BLF:kh

130 Endorsed: Mailed Apr 12 1938

Div. 6 Room 4898C T:hw Paper No. 11

Department of Commerce
United States Patent Office
Washington

Applicant: E. C. Britton et al Ser. No. 44,252 Filed Oct. 9, 1935 For Production of Alkyl Halides

Griswold & Burdick
c/o The Dow Chemical Co.
Midland, Mich.

Responsive to amendment filed Apr. 1, 1938.

Claims 22 to 34 are each rejected on the same grounds as were claims 3, 8, 9, 10, and 13 to 21 in the last Office action,

i. e., as being unpatentable over Nutting #2,007,144 in view of Curme #1,518,182. Applicants' arguments have been carefully considered, but the examiner still considers the rejection to be sound. This rejection was treated at some length in the prior Office action, and no further discussion is seen to be necessary.

An issue has been reached, and this action is made final.

A M LEWERS
W.T. *Examiner*

131 Endorsed: Mail Division Sep 30 1938 U. S. Patent Office

Endorsed: Board of Appeals Oct 3 - 1938 U. S. Patent Office

Endorsed: Paper No. 12 Oct 4 1938 Division 6

In the United States Patent Office
Before the Board of Appeals

Applicant E. C. Britton et al.
Serial No. 44,252
Filed October 9, 1935
For "Production of Alkyl Halides"

Appeal to the Board of Appeals from a Decision of the Primary Examiner

Now comes the applicant Britton et al. by his attorneys undersigned and appeals to the Board of Appeals from the final rejection rendered April 12, 1938 by the Primary Examiner of claims 22-34, inclusive, of the above-identified patent application.

The following are the grounds upon which the appeal is taken:

1. That the Examiner erred in his interpretation of the references.

2. That the Examiner erred in his application of the references as bearing upon the claims.

3. That the Examiner erred in rejecting claims 22-34, inclusive, as being unpatentable over the references.

4. That the Examiner erred in not allowing the claims of the application.

The appeal fee of Fifteen Dollars ($15.00) is enclosed.

Respectfully submitted,

GRISWOLD & BURDICK
Attorneys for Britton et al.

Midland, Michigan
September 29, 1938

132 Endorsed: Paper No. 12 Oct 6 1938 Division 6

Endorsed: Mail Division Sep 30 1938 U. S. Patent Office

Griswold and Burdick
Patent Department
The Dow Chemical Company
Midland, Michigan

Case 1074

Midland, Michigan, September 27, 1938

Inventors Edgar C. Britton, Carl F. Prutton, and Jack L. Williams
Title "Production of Alkyl Halides"
Serial No. 44,252
Filed October 9, 1935

Allowed ....
Patent to be Issued to ....

Commissioner of Patents,
Washington, D. C.

Sir:—

In connection with the above entitled case, please apply the enclosed remittance in payment of Patent Office fees in the amounts and for the purpose below indicated:

Patent
Design } Application Filing Fee ....
Trade-Mark

Assignment Record Fee ....
Patent Application Final Fee ....

Appeal to Board of Appeals Fifteen Dollars ($15.00)
Remarks:

kh

Respectfully,

GRISWOLD AND BURDICK,
Attorneys.

ECB

133 Endorsed: Mailed Oct 14 1938

T:hw Paper No. 13

Department of Commerce
U. S. Patent Office
Washington, D. C.

In re application of E. C. Britton et al Serial No. 44,252
Filed October 9, 1935 For: Production of Alkyl Halides

On Appeal Before The Board of Appeals

Examiner's Statement

This is an appeal from the final rejection of claims 22 to 34. No claim has been allowed.

The appealed claims are as follows:—

22. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

23. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chloroethane derivative having a boiling point higher than that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

24. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chloroethylene derivative having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C. and under approximately atmospheric pressure.

134 25. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachlorethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

26. In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

27. In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachlorethane and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

28. In a process for the production of ethyl chloride, the step which consists in passing, in substantially equimolecular proportions, ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of tetrachloroethylene and aluminum chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

29. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

135 30. In a process for the production of ethyl chloride, the steps which consist in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

31. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the step which consists in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

32. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic

liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

33. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hy-
136 drocarbons having a boiling point above 40° C., while
the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl chloride product substantially as formed.

34. In a process for the production of an ethyl monohalide selected from the group consisting of ethyl chloride and ethyl bromide, the steps which consist in passing ethylene and a hydrogen halide selected from the group consisting of hydrogen chloride and hydrogen bromide, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum halide and an organic liquid selected from the group consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above 40° C., while the bath is maintained at a temperature between 12° and 40° C., and under approximately atmospheric pressure, and continuously distilling off ethyl halide product substantially as formed.

The Invention

The invention relates to the preparation of alkyl halides and more particularly to the preparation of alkyl chlorides. The products are prepared by the direct addition of hydrogen halide to an olefine. The process is carried out continuously by passing equimolar proportions of olefine and hydrogen halide through a liquid medium consisting of a halogenated aliphatic hydrocarbon and an aluminum halide, at a temperature above the boiling point of the alkyl halide produced. Use of this elevated temperature results in the vaporization of the alkyl halide and its consequent separation from the reaction zone. In this manner the reaction can be carried out continuously; the olefine and hydrogen halide being passed into the reaction medium and the alkyl halide being removed from the reaction zone as a vapor.

Applicants specifically (Example 2) disclose the preparation of ethyl chloride. A reaction medium consisting
137 of anhydrous tetrachlor-ethylene and anhydrous aluminum chloride was maintained at 25° C. Ethylene gas and hydrogen chloride gas, in substantially stoichiometrical proportions, were passed into the reaction medium. Ethyl chloride was produced and passed off the top of the reaction chamber as a vapor which vapor was subsequently condensed and collected. A yield of 97% of theoretical was obtained.

The References

Curme	1,518,182	Dec. 9, 1924
Nutting et al	2,007,144	July 2, 1935

Curme discloses a process of making ethyl chloride by reacting ethylene and hydrogen chloride in the presence of aluminum chloride as a catalyst.

Nutting et al disclose a process of making ethylidene chloride by passing a gaseous mixture of vinyl chloride and hydrogen chloride into a bath consisting of aluminum chloride suspended in an organic liquid such as trichlor-ethane or tetrachlor-ethane. Nutting et al state that the bath may be maintained at a temperature at which the ethylidene chloride produced is vaporized, page 1, col. 2, line 52, to page 2, col. 1, line 17. Thus the process is carried out continuously, the vinyl chloride and hydrogen chloride being continuously passed into the catalytic bath and the product being continuously withdrawn as a vapor.

The Rejection

All the claims (22 to 34) were each rejected as being unpatentable over Nutting et al in view of Curme. The examiner considers that it would be an obvious expedient in view of Curme to substitute ethylene for vinyl chloride in the basic process of Nutting et al.

138 Nutting et al disclose a process of preparing ethylidene chloride by passing a gaseous mixture of vinyl chloride and hydrogen chloride into a bath consisting of

aluminum chloride suspended in a chlorinated-hydrocarbon solvent. The bath is maintained at such a temperature that the ethylidene chloride formed passes off as a vapor and thus the process is carried out continuously. The reaction occurs in the following manner:

$$CH_2{=}CHCl + HCl \longrightarrow CH_3{-}CHCl_2.$$

It is thus apparent that the reaction is an addition of HCl to the olefinic double bond in the vinyl chloride.

Curme discloses a process of making ethyl chloride by reacting ethylene and hydrogen chloride in the presence of aluminum chloride as a catalyst. The reaction occurs in the following manner:—

$$CH_2{=}CH_2 + HCl \longrightarrow CH_3{-}CH_2Cl.$$

It is thus apparent that the reaction is an addition of HCl to the olefinic double bond of ethylene.

The examiner considers that a person skilled in the art would realize that the process of Nutting et al could be adapted to the preparation of ethyl chloride. Such a person would realize that a process for the addition hydrogen chloride to vinyl chloride could be used for addition of hydrogen chloride to ethylene. To combine the teaching of Curme with that of Nutting et al would be merely trying out a process which is suggested by the prior art and would involve no invention, In re Wietzel & Michael, 400 O. G. 463. An inspection of the two references will reveal how closely related are the two processes. Both references dis-
139 close the addition of hydrogen chloride to a compound containing an olefinic double bond. Nutting et al disclose adding hydrogen chloride to vinyl chloride and Curme discloses adding hydrogen chloride to ethylene. These compounds are so closely related that a person skilled in the art would realize that a process for adding hydrogen chloride to vinyl chloride could be used for adding hydrogen chloride to ethylene. Ethylene has the formula $CH_2{=}CH_2$, and vinyl chloride has the formula $CH_2{=}CHCl$. Thus it is apparent that both compounds have a reactive olefinic bond. A person who would be investigating the addition of hydrogen chloride to various compounds would understand that the reactive group in each case is the olefinic double bond. The fact that vinyl chloride has one hydrogen substituted

by chlorine would be understood as not interfering or affecting the addition reaction.

For the reasons set out above the examiner considers that the rejection should be affirmed.

Respectfully,

A M LEWERS
Examiner, Division 6.

Attorneys:

Griswold & Burdick
c/o The Dow Chemical Co.
Midland, Mich.

140

Paper No. 14
28398

Department of Commerce

United States Patent Office

Washington

October 21, 1938

Sir:

The case of Edgar C. Britton et al Serial No. 44,252, will be heard by the Board of Appeals on the 29th day of March, 1939.

The hearings will commence at 9:30 A. M. and as soon as the argument in one case is concluded the succeeding case will be taken up.

If any party, or his attorney, shall not appear when the case is called, his right to an oral hearing will be regarded as waived.

The time allowed for arguments is as follows:

Ex parte cases, thirty minutes;

Interpartes appeals: Interlocutory and final hearings when no testimony has been taken, thirty minutes each side; final hearing when testimony has been taken, one hour each side.

By special leave, obtained before the argument is commenced, the time may be extended.

The appellant shall have the right to open and conclude in interpartes cases, and in such cases a full and fair opening must be made.

Briefs in interpartes appeals must be filed in accordance with the provisions of Rules 144 and 163, as amended.

Respectfully,
CONWAY P. COE
Commissioner of Patents.

To Messrs. Griswold & Burdick
c/o The Dow Chemical Co.
Midland, Mich.

141 Endorsed: Board of Appeals Mar 29 1939 U. S. Patent Office

#15

Department of Commerce

In the United States Patent Office

On Appeal Before the Board of Appeals

In re Application of
E. C. Britton et al
Serial Number 44 252
Filed 1935 October 9
For "Production of Alkyl Halides"

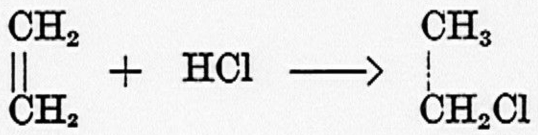
Brief For Britton et al

This is an appeal from a decision of the Primary Examiner finally rejecting claims 22 to 34 of the above-identified application, which are all of the claims pending therein.

Claim 22 is representative of the appealed claims:

"In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure."

The subject matter of the invention is an improvement in the known process of making an ethyl halide, e. g., ethyl chloride, by reacting ethylene with hydrogen chloride, thus:



$$\begin{array}{c}CH_2\\ \| \\ CH_2\end{array} + HCl \longrightarrow \begin{array}{c}CH_3\\ | \\ CH_2Cl\end{array}$$

Ethylene contains an unsaturated double bond to which hydrogen chloride is additively joined to form the saturated compound, ethyl chloride. The addition of a hydrogen halide to an unsaturated double bond is one of the familiar type reactions in organic chemistry. Depending upon the character of the compound in which the double bond occurs however, there is a great diversity in the conditions
142 under which the reaction is caused to take place. In some cases the reaction proceeds much more easily than in others. The simplest compounds containing a double bond are the olefines, which are hydrocarbons having the general formula C_nH_{2n}. Thus ethylene, the first member of the series, has the formula C_2H_4, propylene C_3H_6, butylene C_4H_8, amylene C_5H_{10}, etc. Hydrogen chloride adds readily to olefines, with the exception of ethylene. For example, the Curme Patent No. 1,518,182, of record, shows that isopropyl chloride is formed with great facility by merely bringing propylene and hydrogen chloride into contact. The reaction of ethylene with hydrogen chloride to form ethyl chloride does not take place readily, and to bring it about the use of high pressure or catalysts, or both, has been found necessary. Various methods have been described for carrying out the reaction, but in the previous methods there have been difficulties due to low yields, formation of by-products or polymerization products, or the rapid deterioration of the catalyst. The use of high pressures is disadvantageous, if it can be avoided.

The present invention discloses an improved method of reacting ethylene and hydrogen chloride with the use of a catalyst, which can be carried out at atmospheric pressure to give high yields of a product of great purity. The catalyst is anhydrous aluminum chloride which is suspended in a liquid medium consisting of a chlorinated lower aliphatic hydrocarbon, examples of which are tetrachloroethane and tetrachloroethylene. The gases, ethylene and hydrogen chloride, are passed into the liquid suspen-
143 sion of the catalyst, where they react to form ethyl chloride. The temperature of the reaction is above 12° C., which is the boiling point of ethyl chloride, but below the boiling point of the liquid medium, so that the product ethyl chloride distills off as it is formed. The claimed

process covers a specific combination of conditions which are necessary to produce good results, thus:

catalyst—aluminum chloride
liquid medium—chlorinated lower aliphatic hydrocarbon boiling above 12° C.
temperature—above 12° C. and below boiling point of liquid medium
pressure—atmospheric

The examples show yields of from 77 to 97 per cent, depending upon the concentration of the ethylene gas and upon variations within the conditions summarized above.

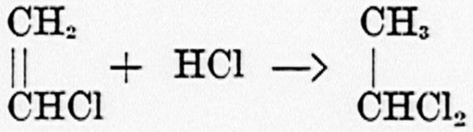
The references on which the rejection is based are the Curme Patent No. 1,518,182 and the Nutting et al Patent No. 2,007,144, the latter being used as the basic reference. Hence the rejection is based upon a combination of references.

Before discussing the references we wish to review the history of this case in the examining division. When the application was filed, certain pertinent art was acknowledged therein, including the Curme Patent No. 1,518,182, which is now relied upon (page 2, line 14). In the first action, Paper No. 2, the Nutting et al patent was cited and an irrelevant Curme Patent No. 1,545,742. Applicants replied. In the second action, Paper No. 4, no references were mentioned, certain formal objections being made to
the terminology in the claims. Applicants endeav-
144 ored to meet these formal objections. In Paper No.
7, an Office action given June 12 of 1937, one year and eight months after the application was filed, seven claims, which were directed to substantially the same subject matter as those now on appeal, were allowed, certain other claims being objected to on the ground that the term "halogen" included elements other than chlorine and bromine, and that the claims should be so limited since Applicants had not shown other than these two halogens. Applicants promptly inserted a Markush expression to overcome this objection. Then, in November of 1937, after the application had been on file for over two years, the Examiner suddenly "discovered" the Curme Patent No. 1,518,182 (which had been mentioned in the specification as filed) and handed down a rejection on the combination of Nutting

et al with this "newly cited" reference. It seems unfortunate that this reference was not earlier cited if it was of sufficient effect to preclude allowance of the claims, and we feel that the Applicants have been unnecessarily subjected to piece-meal action by the examining division.

It is appreciated that the reaction of the Board to this
plaint may be, and properly should be, to the effect that the
situation is an unfortunate one for the Applicants, but that
if the references actually meet the claims it is a happy circumstance
the Office did not issue an invalid patent. Our
only reason for calling attention to the course of the examination
is to show that the question of anticipation here
is an extremely doubtful one, and was in fact highly
145 debatable in the Examiner's mind. It took the Examiner
more than two years to arrive at the view
that the Curme patent affected the patentability of the claims herein. Even then, the final rejection was based on a combination of references which lacks the settled requirement of a suggestion in either reference to make the combination. Apparently the Examiner had lived with the application so long that the suggestion was drawn therefrom. The Board will recognize the impropriety of this type of rejection.

As to the references, the basic reference, Nutting is not concerned with the reaction of ethylene and a hydrogen halide to produce an ethyl halide, such as ethyl chloride. The patent describes a method for making ethylidene chloride by reacting vinyl chloride with hydrogen chloride. Vinyl chloride is an unsaturated compound having a double bond to which hydrogen chloride adds, thus:



$$\begin{array}{l}CH_2\\ \| \\ CHCl\end{array} + HCl \longrightarrow \begin{array}{l}CH_3\\ | \\ CHCl_2\end{array}$$

Hence the starting material is different, the product is different, and conditions for carrying out the reaction permit a much wider latitude of choice than the present inventors have found applicable in their process for making ethyl chloride. Nutting passes the vapors of vinyl chloride and hydrogen chloride gas into a bath composed of aluminum chloride catalyst suspended in a non-aqueous liquid medium. This liquid medium can be any one of a variety of substan-

ces, such as vinyl chloride itself, or ethylidene chloride, the product of the reaction, or naphtha or chlorinated hydrocarbons, thus giving a considerable range of choice. The examples of the patent show the use of vinyl chlo-
146 ride and ethylidene chloride, i. e., either the starting compound or the product of the reaction. The reference to other solvents is simply by way of generalization, the natural conclusion being that the first-named solvents are preferred. Nutting uses a temperature from —10° to 135° C., which covers a range from much below the boiling point of the product to a point considerably above it or above that of the liquid medium. Here again a wide range of choice is presented. Nutting's method is carried out either under pressure in an autoclave or at atmospheric pressure. Evidently, as shown by three of his examples, it is preferred to operate as a batch process in an autoclave under superatmospheric pressure, using vinyl chloride itself as the liquid medium. In one example, when atmospheric pressure is used, the product is not distilled out continuously as formed, but only after the reaction is finished, although the patent mentions such continuous form of operation as being possible. At all events, the patent shows a process for making a different compound than the one covered by the present Applicants' claims, and it shows a much wider range of operating conditions than the Applicants'. This range, it is true, includes conditions similar to those in Applicants' process, but they are not preferred by Nutting, in fact are merely given as alternatives by way of widening the scope of the patent disclosure. Certainly there is nothing in the patent to show which combination of conditions out of the many possible ones shown should or could be used in a process for making ethyl chloride.

147 The Curme patent discloses a process of making ethyl chloride by reacting ethylene and hydrogen chloride in vapor phase in the presence of aluminum chloride as catalyst under high pressure. The patent says a substantial quantity of ethyl chloride is produced without pressure, but commercial yields are obtainable at pressures "no higher than 35 atmospheres". Apparently Curme did not regard this as a high pressure, but as a matter of fact any chemist knows that there is a vast difference between

operating at atmospheric pressure and at a pressure of more than 500 pounds per square inch. For usual purposes this is high pressure. In the customary manner, by way of generalization and broadening the scope of his patent, Curme adds as an afterthought that his "invention is not limited to a reaction between the vapor phases of the combining substance as these may react in solution. The solvent employed may be the reaction product, or other suitable solvent, preferably anhydrous." (Lines 70-75.) In other words, the patentee did not want to be limited to his invention as he described it, but wished to cover other ways of producing the result, and hazarded some prophetic statements as to how this might be done. Such prophetic statements, merely proposing a problem rather than showing a solution of it, have often been held insufficient as an anticipation of a later invention which actually described the means and conditions for solving the problem. In any case the bare suggestion of using a solvent by Curme is not sufficient to teach or suggest the Applicants' invention. All
that Curme shows is that the reaction of ethylene and
148 hydrogen chloride in the vapor phase and in the
presence of aluminum chloride as catalyst must be carried out at pressures on the order of 35 atmospheres to produce commercial yields of ethyl chloride. If any deduction were to be made from his prophetic statement about the use of a solvent, it would be to the effect that pressure was also necessary when a solvent is used. Furthermore, Curme suggests no solvent other than the reaction product.

In his rejection the Examiner has expressed the opinion that a person skilled in the art, a chemist, would realize that the Nutting method could be used to make ethyl chloride, and that combining Curme with Nutting suggests all that Applicants have shown. This is clearly reasoning a posteriori, wherein the Examiner, after reading the Applicants' disclosure, turns to Nutting and Curme, picks out an element from this patent, another from that, and finally makes out the combination of Applicants' claims. This is neither a fair nor proper method of building up a basis for rejection. It is like solving a problem by copying the answer from a book. The Board has frequently refused to approve this kind of a rejection.

To decide whether or not invention is present in a situation like this, the question has to be answered: What was the state of the art at the time Applicants made their invention? Now, the elements of Applicants' claims can be found in Nutting or Curme indiscriminately mixed with a large number of other facts which are irrelevant to this invention, like the scrambled pieces of several picture puzzles all mixed together. Would it be obvious to a chemist to select a piece here, another there, out of the mass to make the right combination to solve his problem?

149 Nutting shows that vinyl chloride and hydrogen chloride can be reacted in a suspension of aluminum chloride as catalyst in a liquid medium within a wide range of temperatures and pressures. But Nutting's preferred conditions are not those which the Examiner has selected in building up the equivalent of Applicants' claims. Not at all. The Examiner selected judiciously other elements which are more or less incidentally mentioned in the patent, because he now knows just which ones to pick out, having already read the answer in Applicants' specification. Nutting does not specifically show the combination of a reaction bath of aluminum chloride and a lower chlorinated aliphatic hydrocarbon having a boiling point above that of his reaction product, and maintaining the temperature above the boiling point of the reaction product, but below that of the liquid medium, whereby the product is distilled off as formed. He merely says that his process might be carried out in some such way if the proper solvent were selected, but he does not tell what kind of a solvent. He names various solvents, naphtha, chlorinated hydrocarbons, the reaction product itself, or the starting material. He prefers to use the starting material or the reaction product as shown by his examples, and when he uses these he does not distill the product off as it forms, but works in an autoclave under pressure, or at a temperature such that the product accumulates in the reaction mixture, and distills it off after the reaction is finished. This is no difficulty for the Examiner, however, because he now knows from Applicants' disclosure that if one wanted to make ethyl chloride by a similar process he would not use Nutting's preferred conditions, but some of the other conditions that Nutting mentions incidentally in broadening his disclosure. The practice has often been condemned of interpreting the references in the light of the specification under consideration, and then combining the references so construed to

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build up a basis for rejection. Knowledge after the fact cannot be used to show that the references mean something different from what is disclosed on their face.

Coming to the Curme patent, here again the Examiner would not use Curme's conditions, but would substitute the different conditions which he has arbitrarily selected from Nutting. He disregards Curme's statement that high pressure is necessary to get commercial yields of ethyl chloride. Here is the kernel of the whole issue. If Nutting were to be combined with Curme to make out an anticipation of Applicants' claims, the whole teaching of Curme is that high pressure would be required. It was not to be expected, therefore, from the teaching of these referencs, that, if a suitable selection of operating conditions were made from Nutting, the reaction of ethylene and hydrogen chloride could be carried out at atmospheric pressure to give a high yield of ethyl chloride. Whatever these references show as respects the formation of ethyl chloride, they do not show that pressure could be dispensed with. This is a new or improved result that is not suggested by the references. It is unexpected in view of the references. There is no basis for holding, then, that it is obvious.

151 It is submitted that it required invention to select from all the many alternatives afforded by the references the particular combination of conditions that together produce Applicants' improved result, enabling them to carry out the continuous production of ethyl chloride at moderate temperatures and without the use of high pressure. If one were to be guided by the references alone, he would not know how to select the proper combination of conditions for Applicants' purpose. When the Applicants, as a result of extensive experimentation, found the right combination, and obtained a result wholly unpredictable from the references, it does not become anyone to say, in retrospect, that it was obvious and did not require invention. Ex parte Alexander, 4 U. S. P. Q. 154; Ex parte Conklin, 11 U. S. P. Q. 151; Ex parte Fothergill, 33 U. S. P. Q. 290.

The several claims on appeal are similar to claim 22 quoted above. Claims 22-25 distinguish from each other in breadth with respect to "chlorinated lower aliphatic hydrocarbon" (claim 22), "chloroethane derivative" (claim 23), "chloroethylene derivative" (claim 24), or specifically

"tetrachlorethane" (claim 25). Claims 26-28 are more specific with respect to the use of ethylene and hydrogen chloride "in substantially equimolecular proportions". Claims 29 and 30 define the liquid medium by a Markush expression "consisting of those chlorinated and brominated lower aliphatic hydrocarbons having a boiling point above that of ethyl chloride", claim 30 distinguishing from claim 29 in the additional step of continuous distillation of the
ethyl chloride product. Claims 31 and 32 are similar
152 similar to 29 and 30, but are slightly broader with
respect to "an ethyl monohalide selected from the
group consisting of ethyl chloride and ethyl bromide". Claims 33 and 34 are limited to a narrower temperature range in "12° to 40° C." All of the claims are limited to carrying out the reaction "under approximately atmospheric pressure", whereas the only reference, Curme, showing the production of ethyl chloride employs high pressure, as already explained. The issue with respect to patentability applies equally to all the claims.

In conclusion, neither of the references singly or combined teach Applicants' specific combination of steps in a method for producing ethyl chloride or ethyl bromide. There is no way of making out the combination of steps from the references except by reconstructing them in the light of Applicants' specification. In fact, the preferred procedures of the reference patents are quite different from the combination of the claims on appeal. There is no suggestion in the references for making the Applicants' specific combination, and certainly no teaching that, if it were used, it would be possible to produce ethyl chloride or ethyl bromide continuously at atmospheric pressure. This was an unobvious and unpredictable result. It is submitted that it required invention to discover Applicants' specific combination which produces an unobvious result. Although the various elements of the claimed combination may be separately found in one or other of the references, they are shown there merely in general statements of a prophetic character, and not in the actual procedures described in the
patents. No suggestion can be found in the refer-
153 ences that would lead a chemist to select the elements
of Applicants' combination. Indeed, the teaching of
the references would direct him away from making such

selection. The citation by the Examiner of in re Wietzel and Michael is not in point, because none of the art shows the specific combination of the claims. There is no showing in the references that the combination would work in the advantageous way that Applicants' have disclosed.

Applicants' improved process has a number of advantages. By avoiding the use of high pressure not only is the operation simplified but also the polymerization of the unsaturated compound, ethylene, is prevented, the formation of undesirable by-products is reduced, and a high yield of product is realized.

Since the references do not show or suggest Applicants' specific combination, or suggest the possibility of obtaining their improved result, the claims are patentably distinct from the cited art and should be allowed.

Respectfully,

GRISWOLD & BURDICK
Attorneys for Britton et al.

E. C. BURDICK
DEAN LAURENCE
Of Counsel

154 U. S. Patent Office Board of Appeals Apr 7 1939
Mailed

Paper No. 16

Appeal No. 28,398 MMS
Hearing: March 29, 1939

In the United States Patent Office

Before the Board of Appeals

Ex parte Edgar C. Britton, Jack L. Williams and Carl F Prutton

Application for Patent filed October 9, 1935, Serial No. 44,252. Production of Alkyl Halides.

Messrs. Griswold & Burdick for applicants.

This is an appeal from the action of the examiner finally rejecting claims 22 to 34, inclusive.

Claim 22 is illustrative and reads as follows:

22. In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

The references relied upon are:

Curme,	1,518,182,	Dec. 9, 1924,
Nutting et al,	2,007,144,	July 2, 1935.

There are altogether too many claims here in view of the
art cited. Applicants point out no material distinc-
155 tions between the claims and select claim 22 as illus-
trative. Their main contention is that Curme indicates that high pressures are necessary. It is our view that Curme has no such teaching when a catalyst is used. See lines 52 to 54, page 1 of Curme.

The process of Nutting et al using vinyl chloride instead of ethylene is substantially what is stated in claim 22 and it is our view that any chemist, with the reference patents before him, would instantly recognize the applicability of the Nutting et al process to the manufacture of ethyl chloride as taught by Curme.

Nutting et al teach the suspension or solution of the catalyst in a chlorinated lower aliphatic hydrocarbon under the conditions of the process of claim 22 and it seems obvious to resort to a similar expedient in the Curme process. See Example No. 1 and page 2, line 31 of Nutting et al.

By this disposition of the catalyst, Nutting et al state that the reaction may be carried out at atmospheric or elevated pressure. Curme indicates that the reaction may be carried out when at room temperature, which is above 12°C.

For reasons indicated above and in the examiner's statement, we do not consider the claims allowable and the decision of the examiner is accordingly affirmed.

BOARD OF APPEALS

EUGENE LANDERS
Examiner-in-Chief

J. W. CLIFT
Examiner-in-Chief

F. G. PORTER
Examiner-in-Chief

April 7, 1939

Messrs. Griswold & Burdick,
c/o The Dow Chemical Company,
Midland, Mich.

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Department of Commerce
United States Patent Office
Washington

Ex parte Edgar C. Britton,
Jack L. Williams, and
Carl F. Prutton,
Serial No. 44,252,
Filed October 9, 1935,
Production of Alkyl Halides.

Notice of Civil Action Under Section 4915 R. S.

A Civil Action under Section 4915 R. S. entitled The Dow Chemical Company v. Conway P. Coe, Commissioner of Patents, Civil Action No. 2924, involving this application, was filed on May 31, 1939, in the District Court of the United States for the District of Columbia.

W. W. COCHRAN
Law Examiner.

May 31, 1939.

5/17/39

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1935

CONTENTS

1. Application papers.
2. Rejection JAN 10 1936
3. Amendment a JUN 19 1936
4. Rejection SEP -3 1936
5. Sub. Power of Atty FEB 25 1937
6. Amendment B FEB 25 1937
7. Rejection JUN 12 1937
8. Amendment C AUG 13 1937
9. Rejection NOV 3 1937
10. Amendment D APR 1 1938
11. Rejection (Final) APR 12 1938
12. Appeal to Board ($15 Pd. SEP 30 1938
13. Examiner's Statement OCT 14 1938
14. Hearing Mar. 29, 1939
15. BRIEF MAR 30 1939
16. DECISION BY BOARD APR -7 1939 (affirmed)
17. Notice of Civil Action under Sec. 4915 R.S. May 31-1939
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20. Not up for Action
21. Do not hold abandoned
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44252

U.S. GOVERNMENT PRINTING OFFICE 1934

158 Filed Oct 28 1940 Charles E. Stewart, Clerk

Department of Commerce
United States Patent Office

To all persons to whom these presents shall come, Greeting:

This Is to Certify that the annexed is a true copy from the records of this office of the Disclaimer, filed May 22, 1940, in the matter of the

Letters Patent of

Howard S. Nutting, Peter S. Petrie and Myron E. Huscher,
assignors to The Dow Chemical Company,

Number 2,007,144, Granted July 2, 1935,

for

Improvement in Methods of Making Ethylidene Chloride.

In Testimony Whereof I have hereunto set my hand and caused the seal of the Patent Office to be affixed, at the City of Washington, this tenth day of June, in the year of our Lord one thousand nine hundred and forty and of the Independence of the United States of America the one hundred and sixty-fourth.

CONWAY P. COE
(Seal) *Commissioner of Patents.*

Attest:
D. E. WILSON
Chief of Division.

159 Mail Division May 22 1940 U. S. Patent Office

Recorded U. S. Patent Office Issue Division May 22 1940 Liber 4 Page 848

In the United States Patent Office

Patentees: Howard S. Nutting et al.
Patent Number: 2 007 144
Issue Date: 1935 July 2
For "Method of Making Ethylidene Chloride"

Hon. Commissioner of Patents
Washington, D. C.

Sir:

Disclaimer

Your petitioner, The Dow Chemical Company, a corporation of the State of Michigan, having its principal office and place of business at Midland, in the County of Midland, State of Michigan, represents that in the matter of a certain improvement in Method of Making Ethylidene Chloride, for which Letters Patent of the United States Number 2 007 144 was granted to Howard S. Nutting, Peter S. Petrie, and Myron E. Huscher, on the 2nd day of July of 1935, it is the assignee of the entire right, title, and interest in and to the invention described in said Letters Patent, said Assignment having been recorded in the Patent Office on 1935 June 6, at Page 131 of Liber K163, and that it has reason to believe that through accident and mistake, and without any fraudulent or deceptive intent, the specification and claims of said Letters Patent are too broad, including inoperative subject matter. Your petitioner, therefore, enters this Disclaimer to the claims in said specification and to that portion of the descriptive matter in said specification to-wit:

160 Claim 6 in its entirety.

From the scope of claims 1, 2, 3, 4, and 5, the use of the method therein claimed in a continuous process wherein ethylidene chloride is distilled from the reaction mixture as it is formed.

From the descriptive proportion of the specification, page 2, column 1, on line 4 beginning:

"A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene cloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed. Any hydrogen chloride and vinyl chloride which pass through the mixture without reacting may readily be separated from the product and recycled in the process. By operating in such manner, the process is made continuous and the quantity of catalyst required to produce a given quantity of catalyst required to produce a given quantity of ethylidene chloride is reduced materially.

THE DOW CHEMICAL COMPANY
(Seal) EARL W. BENNETT
Vice President

Attest:
L. A. CHICHESTER
Asst. Secretary

STATE OF MICHIGAN
County of Midland, ss:

On this 20 day of May, 1940, before me, a Notary in and for the County and State aforesaid, personally came Earl W. Bennett and L. A. Chichester to me known, who, being by me duly sworn, did depose and say that they are, respectively, the Vice President and Asst. Secretary of The Dow Chemical Company, the corporation described in and which executed the foregoing instrument; that they know the seal of said corporation; that the seal affixed to
161 said instrument is such corporate seal; and that the foregoing instrument is the free and corporate act and deed of said The Dow Chemical Company and their free act and deed as officers thereof.

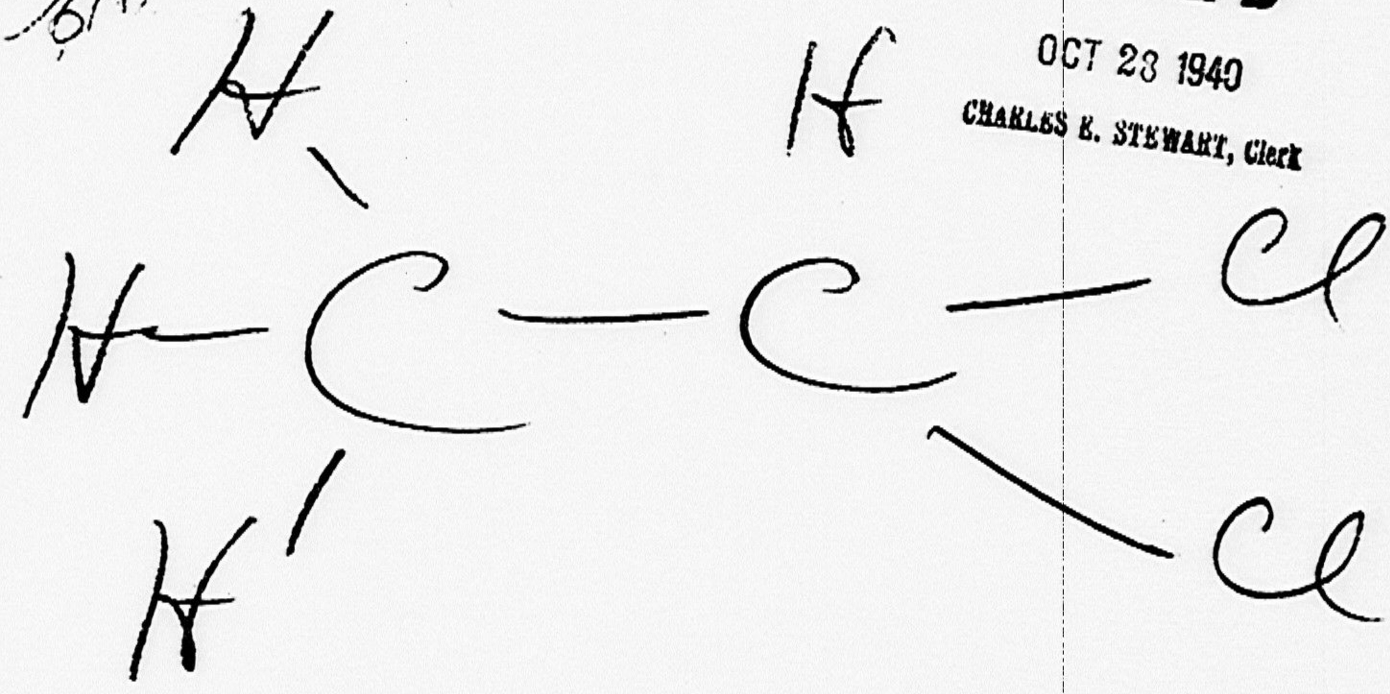
In witness whereof I have hereunto set my hand and affixed my official seal at Midland, Michigan, this 20 day of May, 1940.

GENEVA SMITH
(Seal) *Notary Public.*

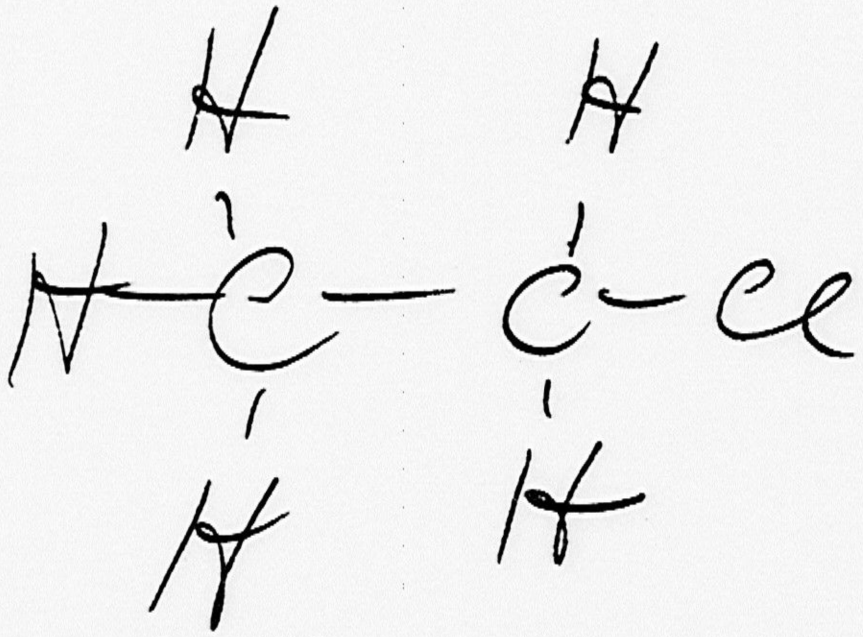
Recorded U. S. Patent Office Issue Division May 22, 1940
Liber 4 Page 850

Pl Exh K EAS 294ca

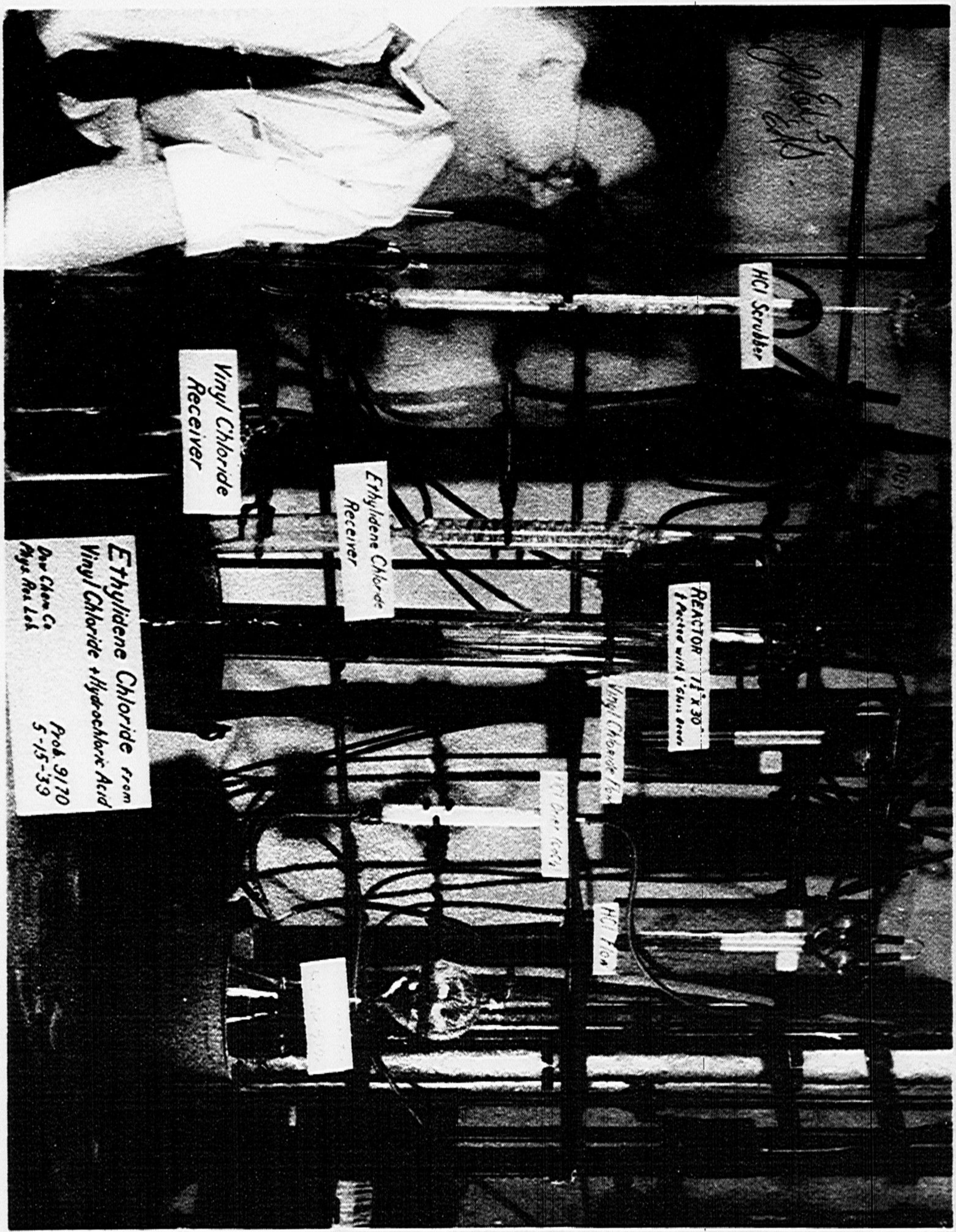
FILED
OCT 28 1940
CHARLES E. STEWART, Clerk



Ethylidene chloride,



Ethyl chloride


Ethylidene Chloride from
Vinyl Chloride + Hydrochloric Acid
Dow Chem Co
Phys Res Lab
Prob. 9170
5-15-39
Vinyl Chloride Receiver
Ethylidene Chloride Receiver
REACTOR 1½" x 30"
Packed with ¼" Glass Beads
Vinyl Chloride Flow
HCl Flow
HCl Scrubber

163 Filed Oct 28 1940 Charles E. Stewart, Clerk

165 Filed Oct 28 1940 Charles E. Stewart, Clerk

The Dow Chemical Company

v.

Coe.

Civil Action No. 2924.

A—Curme,	1,518,182
B—Nutting et al.,	2,007,144
C—Examiner's Statement,	
D—Decision of Board of Appeals.	

Patented Dec. 9, 1924. **1,518,182**

UNITED STATES PATENT OFFICE.

GEORGE O. CURME, JR., OF CLENDENIN, WEST VIRGINIA, ASSIGNOR TO CARBIDE & CARBON CHEMICALS CORPORATION, A CORPORATION OF NEW YORK.

PROCESS OF MAKING ALKYL CHLORIDES.

No Drawing. Application filed May 17, 1922. Serial No. 561,715.

To all whom it may concern:

Be it known that I, George O. Curme, Jr., a citizen of the United States, residing at Clendenin, West Virginia, have invented certain new and useful Improvements in Processes of Making Alkyl Chlorides, of which the following is a specification.

This invention relates to the production of alkyl chlorides.

Alkyl chlorides, especially those corresponding to the simpler alkyl groups, such as ethyl and isopropyl chlorides, are volatile, non-corrosive liquids of agreeable odor, having a high solvent power for oils, fats and many other substances. They are useful for many purposes, for example as solvents, as alkylating agents, and as refrigerants.

Heretofore, these compounds have been prepared by methods which lack simplicity and cheapness. For example, ethyl chloride is now prepared by heating ethyl alcohol with aqueous hydrochloric acid in an autoclave, or in the presence of calcium chloride. Aqueous hydrochloric acid is very corrosive to most metals, so that a costly apparatus is required.

I have now discovered a method by which alkyl chlorides may be obtained by the union of olefines with hydrochloric acid. The reaction may be carried out under anhydrous conditions, preventing corrosion of metals by the acid.

Isopropyl chloride is formed in this way with great facility, the reacting materials being merely brought into contact. Anhydrous gaseous materials may be used, and in this case, an increased pressure in the reaction vessel is desirable, as the yield of chloride is thereby improved and the capacity of an apparatus of given size is increased. Subjecting the mixed gases in approximately their combining proportions to a pressure of 15 atmospheres has given good yields and heating is unnecessary, though not precluded.

Ethylene does not combine with hydrochloric acid as readily as propylene, and with ethylene high pressures or the presence of a catalyst are required if any substantial yield is to be obtained. Pressures up to 160 atmospheres, without a catalyst, and aluminum chloride as a catalyst, without pressure, have each been tried. In either case ethyl chloride is produced in substantial quantity.

The best method for producing ethyl chloride employs both a catalyst and pressure. In the presence of aluminum chloride and at pressures no higher than 35 atmospheres, commercial yields are obtainable, even at room temperature.

When working under anhydrous conditions, any of the reacting materials which fail to combine may be separated from the desired product with the greatest facility because of the great difference in volatility. No substances corrosive to metals are present at any stage, and iron apparatus may be used.

No special form of apparatus is required for carrying out the process. The invention is not limited to a reaction between the vapor phases of the combining substance as these may react in solution. The solvent employed may be the reaction product, or other suitable solvent, preferably anhydrous.

I claim:—

1. Process of making alkyl chlorides which comprises causing hydrochloric acid to react on olefines under anhydrous conditions and under superatmospheric pressure.

2. Process of making alkyl chlorides which comprises causing hydrochloric acid to react on olefines under anhydrous conditions and superatmospheric pressure, and in the presence of aluminum chloride.

3. Process of making ethyl chloride which comprises causing anhydrous hydrochloric acid to react on ethylene, under superatmospheric pressure and in the presence of aluminum chloride.

In testimony whereof, I affix my signature.

GEORGE O. CURME, Jr.

UNITED STATES PATENT OFFICE

2,007,144

METHOD OF MAKING ETHYLIDENE CHLORIDE

Howard S. Nutting, Peter S. Petrie, and Myron E. Huscher, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Michigan

**No Drawing. Application March 8, 1934,
Serial No. 714,656**

9 Claims. (Cl. 260—162)

This invention concerns an improved method of making ethylidene chloride by reacting hydrogen chloride with vinyl chloride in the presence of a catalyst.

It is known that hydrogen chloride and vinyl chloride can be reacted in vapor phase in the presence of solid aluminum chloride as catalyst to form ethylidene chloride, as disclosed in United States Patent No. 1,900,276, in which an approxi-

olecular gaseous mixture of said re-

chloroethane, acetylene tetrachloride, etc., may be employed, if desired.

The hydrogen chloride and vinyl chloride reactants may be employed in any desired proportions, but we prefer to employ an excess of hydrogen chloride, since it is the least expensive of said reactants. The catalyst may also be employed in any desired proportion, but the reaction occurs most rapidly when at least 1 gram of catalyst is used per 100 grams of vinyl chloride. We

to avoid the use of more than 6 grams of

DISCLAIMER

2,007,144.—*Howard S. Nutting*, *Peter S. Petrie*, and *Myron E. Huscher*, Midland, Mich. METHOD OF MAKING ETHYLIDENE CHLORIDE. Patent dated July 2, 1935. Disclaimer filed May 22, 1940, by the assignee, *The Dow Chemical Company*.

Hereby enters this disclaimer to the claims in said specification and to that portion of the descriptive matter in said specification to wit:

Claim 6 in its entirety;

From the scope of claims 1, 2, 3, 4, and 5, the use of the method therein claimed in a continuous process wherein ethylidene chloride is distilled from the reaction mixture as it is formed.

From the descriptive portion of the specification, page 2, first column, beginning in line 4—

"A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed. Any hydrogen chloride and vinyl chloride which pass through the mixture without reacting may readily be separated from the product and recycled in the process. By operating in such manner, the process is made continuous and the quantity of catalyst required to produce a given quantity of ethylidene chloride is reduced materially."

[*Official Gazette June 18, 1940.*]

Broadly, our method consists in

suspending the catalyst, aluminum or ferric chloride, in a non-aqueous liquid medium and thereafter reacting the hydrogen chloride and vinyl chloride in the resultant mixture at between about 10° and 135° C., preferably between 15° and 60° C. The liquefied reactant, vinyl chloride, or the product, ethylidene chloride, is preferably employed as the reaction medium, since the reaction occurs smoothly and rapidly in the presence of either of said compounds and their use simplifies the step of purifying the product. However, other non-reactive solvents, e. g. tri-

stand, preferably with agitation,

in order to assure substantially complete reaction. Any vapors present are then released from the autoclave and collected, after which the reaction mixture is removed and treated with water to render the catalyst inactive. The ethylidene chloride product is separated by distillation, preferably with steam.

Instead of using the liquefied reactant, vinyl chloride, as the reaction medium, other non-aqueous solvents which boil at above room temperature, e. g. naphtha, trichloro-ethane, acetylene

tetrachloride, ethylidene choride, etc., may be empoyed, in which case the reaction may be carried out either at atmospheric or at an elevated pressure. A convenient mode of operation is to mix the aluminum or ferric chloride catalyst with ethylidene chloride, pass hydrogen chloride and vinyl chloride simultaneously into the mixture, and distill the ethylidene chloride product directly from the reaction mixture either periodically or as it is formed. Any hydrogen chloride and vinyl chloride which pass through the mixture without reacting may readily be separated from the product and recycled in the process. By operating in such manner, the process is made continuous and the quantity of catalyst required to produce a given quantity of ethylidene chloride is reduced materially.

The following examples illustrate several ways in which the principle of our invention has been applied, but are not to be construed as limiting the invention.

Example 1

4 grams of aluminum chloride was added to 231 grams of ethylidene chloride and gaseous hydrogen chloride and vinyl chloride were simultaneously passed into the mixture, each at a rate of 300 cubic centimeters per minute, for a period of 2 hours, the mixture being maintained at approximately 25° C. during the operation. After the reaction was completed, the reacted mixture was steam distilled to separate the ethylidene chloride product. Approximately 8 per cent of the vinyl chloride employed was recovered during said distillation. The yield of ethylidene chloride was approximately 85 per cent of theoretical, based on the quantity of vinyl chloride consumed in the reaction.

Example 2

An iron bomb was cooled to -80° C., charged with 2 grams of anhydrous aluminum chloride, 134 grams (2.14 moles) of liquid vinyl chloride, and 50 grams (1.37 moles) of anhydrous hydrogen chloride, and was then closed. The bomb was agitated continuously and permitted to warm slowly to about 11° C., when a violent reaction occurred accompanied by a sudden rise in temperature and pressure. The reaction was substantially complete within a few moments, as indicated by a sharp pressure drop, but in order to assure complete reaction the mixture was permitted to remain in the bomb for about 1 hour. The charge was then removed and steam distilled whereby 134 grams (1.36 moles) of substantially pure ethylidene chloride was obtained. The yield of ethylidene chloride was 99 per cent of theoretical, based on the quantity of hydrogen chloride used.

Example 3

An autoclave provided with an inlet for hydrogen chloride was cooled to approximately -80° C. and charged with 1.5 grams of aluminum chloride and147.5 grams (2.36 moles) of liquid vinyl chloride. The autoclave was then sealed, warmed to room temperature, and 77 grams (2.11 moles) of anhydrous hydrogen chloride was gradually charged therein under pressure at such rate as to maintain the mixture at a temperature between 34° and 44° C. After the reaction was complete the pressure on the bomb was released and the gaseous unreacted hydrogen chloride and vinyl chloride evolved was collected. The liquid reaction mixture was steam distilled to separate the ethylidene chloride product and a small additional quantity of unreacted vinyl chloride. The aqueous layer of the distillate and the liquor remaining in the still were each analyzed to determine the hydrogen chloride contained therein. There was obtained from the reacted mixture 177 grams (1.79 moles) of ethylidene chloride, 20.2 grams (0.32 mole) of unreacted vinyl chloride, and 7.7 grams (0.21 mole) of unreacted hydrogen chloride. The yield of ethylidene chloride was 94 per cent of theoretical, based on the quantity of hydrogen chloride consumed in the reaction.

Example 4

An autoclave provided with an inlet for hydrogen chloride was cooled to about -80° C., charged with 9 grams of ferric chloride and 151.5 grams (2.44 moles) of vinyl chloride, and closed. The autoclave was then warmed to room temperature and 108 grams (2.96 moles) of gaseous hydrogen chloride was passed slowly thereinto under pressure at such rate as to maintain the mixture at a temperature between 30° and 41° C. The reacted mixture was then removed from the autoclave and steam distilled, whereby 226 grams (2.28 moles) of ethylidene chloride was separated. The yield of ethylidene chloride was 94 per cent of theoretical, based on the quantity of vinyl chloride employed.

Example 1 above illustrates the preparation of ethylidene chloride at atmospheric pressure by passing gaseous hydrogen chloride and vinyl chloride into a mixture of aluminum chloride and a non-aqueous liquid medium.

Example 2 shows that by carrying the reaction out under pressure, ethylidene chloride can be produced in practically quantitative yield. However, the same example shows that when the entire reaction mixture is initially charged into a reactor, the reaction which occurs is liable to be violent.

Example 3 illustrates control of the reaction by initially charging an autoclave with liquefied vinyl chloride and aluminum chloride and thereafter introducing the hydrogen chloride reactant under pressure at the rate necessary to maintain the desired reaction temperature.

Example 4 illustrates the use of ferric chloride to catalyze the formation of ethylidene chloride by our method.

Although the reaction is preferably carried out at a temperature below 60° C., since ethylidene chloride is produced in maximum yield with minimum by-product formation at the lower reaction temperatures, the reaction may be carried out at temperatures as high at 135° C. Due to by-product formation, commercial operation at above 135° C. is impracticable.

The hydrogen chloride and vinyl chloride reactants employed in our process may conveniently be produced by cracking ethylene chloride, e. g. by passing ethylene chloride vapors through an iron tube heated to between 400° and 500° C. The resultant hydrogen chloride and vinyl chloride mixture may then be reacted to produce ethylidene chloride by the procedure hereinbefore described. By operating in such manner, ethylidene chloride may be produced in good yield and at low cost from its isomer, ethylene chloride.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. In a method of making ethylidene chloride wherein hydrogen chloride is reacted with vinyl chloride in the presence of a catalyst selected from the class consisting of aluminum chloride and ferric chloride, the improvement which consists in carrying the reaction out in non-aqueous liquid phase.

2. In a method of making ethylidene chloride, the step which consists in reacting hydrogen chloride with vinyl chloride in non-aqueous liquid phase and in the presence of a catalyst selected from the class consisting of aluminum chloride and ferric chloride at a temperature between about 10° and about 135° C.

3. In a method of making ethylidene chloride, the step which consists in reacting hydrogen chloride with vinyl chloride in non-aqueous liquid phase and in the presence of a catalyst selected from the class consisting of aluminum chloride and ferric chloride at a temperature between about 15° and about 60° C.

4. In a method of making ethylidene chloride, the steps which consist in mixing a catalyst selected from the class consisting of aluminum chloride and ferric chloride with ethylidene chloride, adding hydrogen chloride and vinyl chloride, and maintaining the resultant mixture at a temperature between about 15° and about 60° C.

5. In a method of making ethylidene chloride, the steps which consist in adding a catalyst selected from the class consisting of aluminum chloride and ferric chloride to sufficient ethylidene chloride to form a thin mixture and passing hydrogen chloride and vinyl chloride simultaneously into the mixture at approximately atmospheric pressure while maintaining said mixture at a temperature between about 15° and about 60° C.

6. In a method of making ethylidene chloride, the steps which consist in passing hydrogen chloride and vinyl chloride, simultaneously and at approximately atmospheric pressure, into a heated mixture of ethylidene chloride and a catalyst selected from the class consisting of aluminum chloride and ferric chloride, distilling ethylidene chloride from the mixture as it is formed, condensing ethylidene chloride from the distilled vapors, and returning any uncondensed vapors to the reaction.

7. In a method of making ethylidene chloride, the steps which consist in charging a reactor with liquefied vinyl chloride, hydrogen chloride, and a catalyst selected from the class consisting of aluminum chloride and ferric chloride, closing the reactor and maintaining the mixture within the closed reactor at a temperature between about 15° and about 60° C.

8. In a method of making ethylidene chloride, the steps which consist in charging a reactor with liquefied vinyl chloride and a catalyst selected from the class consisting of aluminum chloride and ferric chloride, closing the reactor and thereafter charging hydrogen chloride into the reactor under pressure at such rate as to maintain the reaction mixture at a temperature between about 15° and about 60° C.

9. In a method of making ethylidene chloride, the steps which consist in charging a reactor with liquefied vinyl chloride and a catalyst selected from the class consisting of aluminum chloride and ferric chloride, closing the reactor, charging hydrogen chloride into the reactor under pressure at such rate as to maintain the reaction mixture at a temperature between about 15° and about 60° C., and thereafter steam distilling ethylidene chloride from the reacted mixture.

HOWARD S. NUTTING.
PETER S. PETRIE.
MYRON E. HUSCHER.

179 United States Court of Appeals for the District of Columbia Filed Nov 29 1940 Joseph W. Stewart, Clerk

In the United States Court of Appeals for the
District of Columbia

Appeal No. 7791.

THE DOW CHEMICAL COMPANY, *Plaintiff Appellant*

vs.

CONWAY P. COE, Commissioner of Patents,
Defendant Appellee

Designation for Printed Record

Clerk of the Court

Please print all of the record transmitted from the District Court in this case except pages 170-178 inclusive, being the "Examiners Statement" and the "Decision of the Board of Appeals" where found in Defendant's Exhibit #1, which matter is a duplication being found in Plaintiff's exhibit certified copy of the file wrapper.

NELSON J. JEWETT
Attorney for Appellant

Attorney for Appellee consents
to this Designation

Signed W. W. COCHRAN

Endorsed on cover: No. 7791 Dow Chemical Co., Appellant, vs. Coe. United States Court of Appeals for the District of Columbia Filed Nov. 22, 1940, Joseph W. Stewart, Clerk.

BRIEF FOR APPELLANT

IN THE

United States Court of Appeals for the District of Columbia

UNITED STATES
COURT OF APPEALS FOR THE
DISTRICT OF COLUMBIA

FILED APR 1 - 1941

Joseph W. Stewart

CLERK

October Term, 1940.

No. 7791

THE DOW CHEMICAL COMPANY, *Appellant,* *vs.* **CONWAY P. COE, Commissioner of Patents,** *Appellee.*	Appeal from the United States District Court for the District of Columbia. Honorable Jennings Bailey, District Judge.

Russell Wiles,
George A. Chritton,
Charles J. Merriam,
2800 Board of Trade Bldg.,
Chicago, Ill.,
Nelson J. Jewett,
Munsey Bldg.,
Washington, D. C.,
Counsel for Appellant.

Chritton, Wiles, Davies & Hirschl,
2800 Board of Trade Bldg., Chicago,
Attorneys for Appellant.
March 27, 1941.

THE GUNTHORP-WARREN PRINTING COMPANY, 210 WEST JACKSON, CHICAGO

JUDGE D. LAWRENCE GRONER
UNITED STATES COURT OF APPEALS
WASHINGTON, D. C.

NOV 1941

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IN THE

United States Court of Appeals for the District of Columbia

OCTOBER TERM, 1940.

No. 7791

THE DOW CHEMICAL COMPANY, *Appellant,* *vs.* **CONWAY P. COE, Commissioner of Patents,** *Appellee.*	**Appeal from the United States District Court for the District of Columbia.** **Honorable Jennings Bailey, District Judge.**

APPELLANT'S BRIEF.

MAY IT PLEASE THE COURT:

JURISDICTIONAL STATEMENT.

This suit was brought in the District Court under Section 4915 R. S. (35 U. S. C. A. 65) to compel the issue of a patent rejected in the Patent Office. The allegations of the bill (Rec. pp. 1-6, inclusive) clearly demonstrate the jurisdictional facts, and these are admitted in the answer (Rec. p. 7). The complaint below was dismissed by the District Court for want of equity.

The suit below being a conventional appeal in equity and the decree being final, this Court obviously has jurisdiction of the appeal.

STATEMENT OF THE CASE.

The appeal being from a final decree denying plaintiff's prayer that the patent issue, this Court has before it for review the whole situation, both as it existed in the Patent Office and in the District Court.

The application is in conventional form and claims a new process for making the old and well known chemical ethyl chloride. The question at issue is the presence or absence of invention in the process, there being no question that the process is new.

The fundamental chemical reaction involved in appellant's process was an old reaction, as will later be shown in detail, but the process in which this old reaction was formerly employed was a batch process, whereas the present process is continuous; and therefore the old process was comparatively much less efficient and much more expensive. The advantages of genuinely continuous processes over batch processes have often been considered by the courts.

In a batch process a given charge of the reagents is put into a vessel and the reaction carried to the end, after which the vessel must be emptied, cleaned up, the products separated, etc.

In a continuous process the reagents are added little by little to a reaction zone, the products are continuously drawn off, and the operation (as in the present case) goes on for weeks or months with no interruption. Practical continuous processes are the ideal types for economical commercial production, and the development of a practical, efficient continuous process is always a very great step forward, as it is in the case at bar.

Although the Patent Office concedes that the present continuous process is new, and of necessity must concede its great commercial superiority, it contends that the process is not inventive because a reaction superficially similar to that here involved was described in the prior art as being capable of continuous operation by a method quite analogous to that here involved.

In the present application, ethyl chloride is continuously made by combining ethylene gas with hydrochloric acid gas. In the prior art reference (the Nutting patent), Nutting's desired end product, ethylidine chloride, was made by combining vinyl chloride with hydrochloric acid gas. The argument of the Patent Office is that ethylene and vinyl chloride are so analogous chemically that it is not inventive to react ethylene with hydrochloric acid gas in the same general manner that was described in connection with a process for reacting vinyl chloride.

The application was prosecuted through the Patent Office without any proofs of the lack of analogy between the two starting materials ethylene and vinyl chloride and the practical dissimilarity of the two reactions, which admittedly have a considerable superficial similarity when only chemical formulae are considered.

In the Patent Office applicant relied wholly upon the broad proposition of law which is deemed to be well established, that prediction may not be relied upon in the abstruse field of chemistry. As will be shown later, the overwhelming weight of authority is to the effect that, in chemistry, reasoning by analogy such as here employed by the Patent Office is extremely dangerous and unreliable. The Federal Courts of Appeals and the Supreme Court have repeatedly sustained patents on new chemical processes despite the existence in the prior art of superficially similar processes. The courts have repeatedly refused to accept chemical prediction as determinative of invention; and, in the prosecution through the Patent Office, it was assumed that the Office would follow the accepted decisions of the courts.

Indeed it might be seriously questioned whether an administrative tribunal like the Patent Office has any authority to set up new legal criteria not accepted by the courts, and similarly it would seem that the Court of Customs and Patent Appeals which, in hearing appeals from the Patent Office, is passing only on administrative acts, is equally bound by the generally accepted rules of law, and is not at liberty, as this Court would be, to qualify or modify them.

However this may be, the Patent Office tribunals *did* depart, as we see it, from the established rules and *did* invoke predictive reasoning by analogy, arguing that it would be obvious to do anything with ethylene which had formerly been done with the superficially analogous material, vinyl chloride.

In the District Court not only was the true rule of law brought to the attention of the Court, but overwhelming evidence was introduced demonstrating that, despite the superficial resemblance of their chemical formulae, the two starting products are widely different in fact and are widely different in their behavior in the two processes here under consideration; that is in the alleged continuous variant of the Nutting process and the admittedly continuous process of the applicant.

It was overwhelmingly shown by uncontradicted evidence that whereas the present process can run for weeks or months continuously and without giving any trouble, the Nutting process will only run for a few hours, at the end of which time the apparatus is clogged up by useless tarry material, and that the Nutting process actually spoils nearly as much material as it usefully transforms. The facts on this point are so destructive of any merit in the Nutting disclosure of the continuous variant of his process that plaintiff (which owns that patent) disclaimed all that part of the Nutting invention before the trial.

In the District Court, the Patent Office not only made the argument advanced by its own tribunals and which we believe unsound, but argued and induced the District Court to find (Rec. p. 48) that Nutting discloses an operative continuous process. The argument there made was that a process is technically operative even though it can be run only a few hours before its own limitations compel its cessation. Perhaps this is a technically sound use of words. Perhaps it may be said that a process is technically continuous if the materials are continuously fed in and the end products are continuously drawn off, and that such a process is technically operative even if it can be run only three or four hours.

There is no need to decide this question, because the Court is not dealing with technical definitions but with actual facts. In our view, there can be no question that a process which will run weeks or months continuously is highly inventive over a process which cannot be run over four hours, even if both are technically operative continuous processes; and it is equally manifest, according to our view, that a process is inventive which transforms practically all of its raw materials into a desired end product when the best reference destroys nearly as much of the raw material as it usefully transforms.

Statutes, Treaties and Regulations Involved.

It is not assumed that the requirement of the rules necessitates the reprinting of such fundamental and well known statutes as those providing what is patentable. The only question involved here is whether the application discloses invention or mere mechanical skill, and it is conceded by everyone that new inventions should be patented and new exercises of mere mechanical skill should not.

The only other statutes involved are the well known provisions permitting review of the Patent Office action in a bill filed in the District Court, and the usual rules of appeal.

Statement of Points.

In the appeal papers (Rec. p. 50) the following points in which the court below erred were set forth:

1. In refusing to authorize and direct the Commissioner of Patents to issue to plaintiff a patent upon the Britton *et al.* application Serial No. 44,252, filed October 9, 1935.

2. In sustaining and adopting the decision of the tribunals of the Patent Office, holding that the Britton *et al.* invention was not patentable in view of the prior art.

3. In failing to hold that the process of the application, though simple, inexpensive and efficient, did ~~not~~ involve invention.

4. In holding that the patent to Curme, No. 1,518,182, and the patent to Nutting *et al.*, No. 2,007,144, constituted sufficient disclosure to justify the rejection of the Britton *et al.* application.

5. In holding that the Nutting *et al.* patent No. 2,007,144 discloses an operative continuous process for the production of ethylidine chloride.

6. In entering the judgment of October 1, 1940, dismissing the complaint with costs against plaintiff, and in holding that said disclosure was sufficient to justify the rejection of the Britton *et al.* application.

Generally speaking, these formal assignments of error in patent cases are of little use to the Court of Appeals. As above stated the sole issue is invention and we assert that there were two fundamental errors made by the District Court. First, the District Court departed from the established rule that anticipation by analogy is not permitted in the abstruse field of chemistry; and, second, the District Court erred in relying on a reference which (if operative at all) is only technically operative, is practically useless, and entirely lacks the result of long time operations and high percentage of conversion attained by the invention of the application at bar.

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ARGUMENT.

Reasoning by Analogy to a Conclusion of Non-Invention in Chemical Cases Is Improper.

On this point undoubtedly the leading case is *Corona Cord Tire Company* v. *Dovan Chemical Corporation,* 276 U. S. 358, decision by Mr. Chief Justice Taft whose wide experience with patent matters both in the Court of Appeals of the Sixth Circuit and on the Supreme Bench lends unusual weight to his pronouncements.

The facts of that case ought to be understood because they demonstrate how strictly the courts follow the rule, despite apparent analogies. As the Court points out (276 U. S. 367), practically all rubber is vulcanized by adding a small amount of sulphur and a considerable amount of filler, and then heating in a mold. Vulcanization can be hastened by adding what is called an accelerator. Among the well known accelerators were a group of organic substances known as guanidines and it was particularly known that triphenylguanidine was an excellent accelerator. Triphenylguanidine is one of the guanidine group in which three phenyl groups have been added.

The patentee's discovery was that diphenylguanidine was superior. The two substances are absolutely identical in their general chemical structure, the only difference being that in one, two phenyl groups have been added, and in the other, three. It was argued that the two substances were so closely analogous chemically that there could be no invention in discovering the suitability of one when the suitability of the other was known. The Supreme Court said (page 368):

"But we can not agree with this view. The catalytic

> action of an accelerator can not be forecast by its chemical composition, for such action is not understood and is not known except by actual test."

The rule that chemistry is so wholly empirical that prediction is unreliable dates back to the decision of the Supreme Court in *Tyler* v. *Boston*, 7 Wallace, 74 U. S. 327. Here the question involved was infringement, but since the things which anticipate, if earlier, infringe if later, and *vice versa,* the rule must apply equally to anticipation. The Court says:

> "The law requires the applicant for a patent-right to deliver a written description of the manner and process of making and compounding his new discovered compound. The art is new and, therefore, persons cannot be presumed to be skilled in it or to anticipate the result of chemical combinations of elements not in daily use."

It also says:

> "This term 'equivalent,' when speaking of machines has a certain definite meaning, but when used with regard to the chemical action of such fluids as can be discovered only by experiment, it only means equally good."

This in the strongest way supports the correct holding of numerous courts that chemistry is so largely empirical that each step forward is a new and independent discovery, not predictable in advance.

This doctrine may be considered a special branch of the more general rule that, in order to anticipate, a reference must lead directly to the patented result without the need for any experiment at all.

When we come to apply this general rule the difference between chemical and mechanical cases is at once apparent. A competent machine designer can lay out a new machine on the drawing-board and it can be foretold with practical certainty that the machine will be operative. The movement of all the parts can be determined on paper, the forces involved can be calculated, and, in nearly every case, practical operativeness can be determined in advance with no need for a model or an operating test. The most intricate and expensive special machines are continually built of commercial size from drawings alone, and they continually are found to do exactly what it was expected they would do.

Chemical processes in this regard are entirely different. While certain manifest chemical analogies may suggest the possibility or even the probability that certain reactions may take place, there is always such a possibility or probability of harmful side or concomitant reactions that it is never safe to proceed commercially without careful tests. The fact that the first operation may succeed does not make it any the less an experiment.

The difference is that, in a mechanical case, the builder knows with practical certainty that the machine will operate as intended, whereas in a chemical case the inventor can never have more than a strong hope; and the practical difference is equally manifest to anyone familiar with modern industry. Full-sized machines of the most intricate character are constantly built from drawings and put into immediate practical operation. Chemical processes, on the contrary, generally go through three stages: first, a laboratory test on a very small scale; second, a so-called semi-commercial operation; and, finally, a full-sized commercial operation. If these steps were not required they would not be universally taken. In the case of a chemical process, the most sanguine experimenter would never dare to commence full-sized commercial operations without preliminary tests, whereas in mechanical cases the preliminary test is constantly omitted altogether.

A typical illustration of the application of the general principle is found in *Toledo Rex Spray Co.* v. *California*

Spray Chemical Co., 268 Fed. 201, 204 (C. C. A. 6th). In that case the prior art clearly disclosed a process for making lead sulphate by adding sulphuric acid to a particular bath containing a lead compound. The patent sued on described and claimed the process of precipitating arsenated lead by adding arsenic acid to precisely the same old bath.

The Court's language was as follows (page 204):

> "While in the light of the invention of the patent it may seem that it would naturally have occurred to one acquainted with the Bell & Fell disclosure to have tried the substitution of arsenic acid for sulphuric acid in making arsenate of lead, the fact remains that in the 40 years which elapsed since Bell & Fell it seems to have occurred to no one to try that experiment. In the light of this fact, and the further fact that mere analogy is not, in chemistry, usually so certain an index as in mechanics (*Naylor* v. *Alsop Process Co.* (C. C. A. 8) 168 Fed. 911, 919, 94 C. C. A. 315; *General Electric Co.* v. *Laco-Philips Co.* (C. C. A. 2) 233 Fed. 96, 103, 147 C. C. A. 166), we are not satisfied to say that it was within the expected skill of the chemist to know that Bell & Fell's process of making sulphate of lead (which may or may not have been employed commercially) was equally available for producing arsenate of lead by the mere substitution of arsenic acid for sulphuric acid."

The Eighth Circuit Court of Appeals expressed the same opinion in *Naylor* v. *Alsop*, 168 Fed. 911 (919):

> "It should also be borne in mind in considering this subject that reasoning by analogy in a complex field like chemistry is very much more restricted than in a simple field like mechanics. This distinction has been frequently recognized by the courts.
>
> > 'Of course, a discovery to be patentable must have the attributes of invention; but the mental operation is somewhat different in one who invents a machine and one who discovers a process. * * * The mere selection of a material, and this, too, by

> a process of exclusion, has been deemed sufficient to sustain patentability, and the patent law abounds in instances in which patents have been upheld where the inventor stumbled upon the discovery in total oblivion of the reason why effect followed cause.' *Badische* v. *Kalle,* (C. C.) 94 Fed. 163.

"We shall not lengthen this opinion by quoting extracts from decisions to illustrate this principle. It was explained and enforced in the following cases: *Celluloid Mfg. Co.* v. *Zylonyte Co.* (C. C.) 35 Fed. 301; *Union Tubing Co.* v. *Patterson Co.* (C. C.) 23 Fed. 79, 82; *King* v. *Anderson* (C. C.) 90 Fed. 500, 504; *Electric Smelting Co.* v. *Carborundum Co.,* 102 Fed. 618, 631, 42 C. C. A. 537; *Hemolin Co.* v. *Harway Co.,* 138 Fed. 54, 56, 70 C. C. A. 480; *U. S. Mitis Co.* v. *Midvale Co.* (C. C.) 135 Fed. 103, 107; *Tannage Co.* v. *Donallan* (C. C.) 93 Fed. 811, 816; *Thomas Co.* v. *Electric Co.* (C. C.) 111 Fed. 923, 930.

"The same principle is admirably illustrated by Lord Justice Vaughan Williams, in his opinion involving the Andrews patent. In discussing the limitation of the doctrine of equivalents in patents based upon a chemical process, he says:

> 'It was urged on behalf of the petitioners that Frichot's patent was an anticipation of Andrews' invention, because all oxidizing agents which liberate nascent oxygen are chemical equivalents, and if you once have a man say, "I propose to bleach flour by nascent oxygen which is liberated from ozone", that is an anticipation of the subsequent patent, which says, "I propose to bleach flour by an oxidizing agent of another character which only operates, and can only operate, by the liberation of nascent oxygen or its equivalent". The answer to this is put in this way: *That you cannot apply the doctrine of mechanical equivalents to a chemical patent,* because you cannot predicate that all oxidizing agents will act in the same way, and cannot, therefore, predicate that in conditioning flour an oxide of nitrogen, or an

> oxidizing agent of the chlorine or bromine type, will act in the same way as ozone or any other oxidizing agent mentioned in Frichot's patent.' 24 Patent, Design & Trade-Mark Cases, 365.
>
> "The learned judge qualifies the language which we have italicized later in the opinion when speaking of the doctrine of equivalents in chemical cases, and states the correct rule with remarkable precision as follows:
>
> > 'The doctrine does apply in cases where, having regard to the subject-matter, it can be truly asserted that one of two or more chemical substances *is well known as producing the same effect on the same subject matter.*' 24 Patent, Design & Trade-Mark Cases, 366.

The view of the second Circuit Court of Appeals is demonstrated in *General Electric Co.* v. *Laco-Philips Co.*, 233 Fed. 96, 103. The patent there in suit covered broadly the modern tungsten-filament electric lamp.

The following brief quotation adequately sets forth the Court's view (page 103):

> "And as the same expert truly says:
>
> > 'Chemistry is essentially an experimental science, and chemical prevision is as impossible today, in spite of the accumulation of the great knowlledge, as it was in former times.' "

A further multiplication of authorities is not necessary. The foregoing amply demonstrate that the true rule governing chemical patents is that the field is so empirical that each new result is an independent discovery and that it is not permissible to reason from the prior art by analogy to the conclusion that the patentee's result might have been predicted in advance.

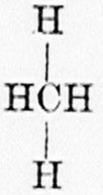
The Patent Office, as we submit, has erroneously departed from rules of law settled both by the Supreme Court and by the leading Courts of Appeals. The departure is natural because following the law leaves the Patent Office Examiners in the chemical divisions but a narrow field in which to exercise discretion and judgment. There is a natural tendency in all government bureaus to seize more and more power, and the departure demonstrated by the decision of the Patent Office in the instant case is rather typical of the expansion of their authority generally demonstrated by government bureaus. The Patent Office examiners, who are primarily technically rather than legally trained, have in cases like the instant one ignored the settled rules of law and have set up some contrary practices of their own. We submit it is the duty of the Patent Office to follow the law wherever it may lead and leave to the courts any alterations which may seem expedient. Unless the courts clearly and definitely reverse the long accepted rules of invention in chemical cases it is the manifest duty of the Patent Office to eschew prediction as a basis for holding anticipation in the chemical classes.

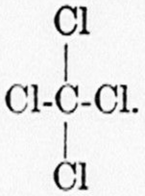
The Chemical Aspects of the Case.

A little elementary chemistry will serve as an introduction to the technical part of the case. This is included only because it is possible that some member of the court either is unfamiliar with chemistry or requires a brief reminder.

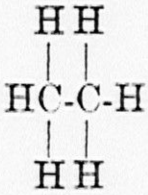
The chemical elements of which all compounds are constituted differ in their ability to hold or attach themselves to other elements. While the element-uniting forces are supposed to be electrical, chemists commonly refer to the elements as having one, two, three or four "bonds", and, in writing the graphic chemical formulae, the bonds are represented as short lines between the literal symbols for the elements.

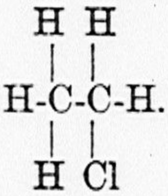
In the instant case, we have to consider but three elements, hydrogen and chlorine, which have one bond each, and carbon, which has four. A simple carbon atom can then hold four atoms of hydrogen, or of chlorine, the compounds so formed being graphically represented as



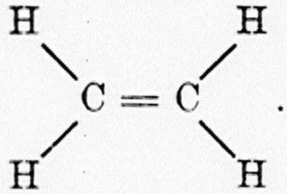
$\begin{array}{c}\text{H}\\|\\\text{HCH}\\|\\\text{H}\end{array}$ and 

$\begin{array}{c}\text{Cl}\\|\\\text{Cl-C-Cl.}\\|\\\text{Cl}\end{array}$

Carbon also has the ability to string atom to atom in chains. We need not here go beyond the simplest chain with but two carbon atoms attached together. This attaching of the two carbon atoms together uses one of the four bonds of each, leaving three bonds on each carbon atom to hold a hydrogen atom. The compound so formed is graphically represented as 

$\begin{array}{c}\text{H H}\\|\;\;|\\\text{HC-C-H}\\|\;\;|\\\text{H H}\end{array}$ and is called ethane. By various chemical processes it is possible to replace a hydrogen atom in ethane with a chlorine atom forming ethyl chloride 

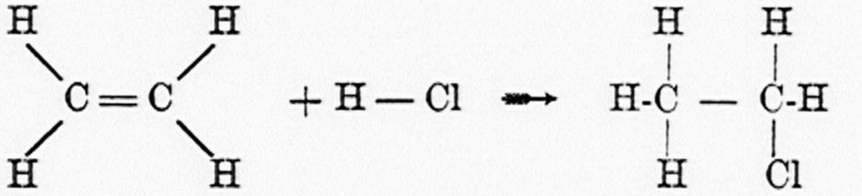
$\begin{array}{c}\text{H H}\\|\;\;|\\\text{H-C-C-H.}\\|\;\;|\\\text{H Cl}\end{array}$ This is the end product made by the process now before the court.

Before turning to the chemistry of the process in issue, another group of compounds must be described. Carbon atoms may be attached together by two bonds, leaving only two of the bonds of each atom to hold hydrogen. The double bond compound thus formed is called ethylene and is represented as  .

This is one of plaintiff's starting materials. It is a gas which is available in considerable quantity. It is a very desirable starting material for many reactions because one of the two bonds between carbon atoms breaks rather easily, affording two free bonds to which other elements or groups of elements may be attached.

Plaintiff's other starting material is hydrochloric acid, H-Cl, which is a gas. Its water solution is the common liquid muriatic or hydrochloric acid of commerce.

The chemical reaction which occurs in plaintiff's process involves the breaking of one of the double bonds of ethylene and the attachment of the H and Cl of hydrochloric acid to the two bonds thus freed to form ethyl chloride. The reaction is represented:



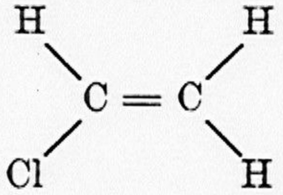
ethylene + hydrochloric acid → ethyl chloride.

This is an old reaction, but it was always carried on as a batch operation under high pressure.

Plaintiff has developed a continuous process operating at atmospheric pressure. In it a suitable solvent is provided and a catalyst (aluminum chloride) is added to it. Then the two gaseous starting materials, ethylene and hydrochloric acid in proper reacting proportion, are bubbled into the solvent liquid. The reaction takes place easily and almost completely. By holding the solvent at a proper temperature the end product, ethyl chloride, boils off as fast as it is formed and is easily collected. Over ninety per cent of the starting materials react, only a very small percentage requiring retreatment.

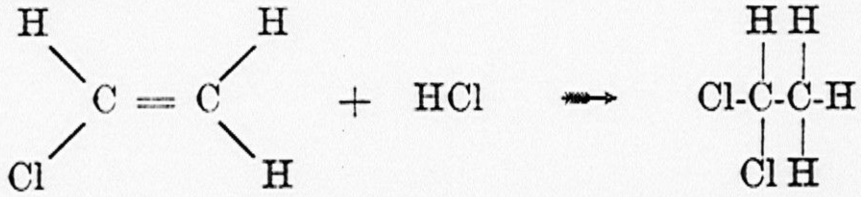
The process operates smoothly and without the formation of any serious amount of useless or objectionable by-products, and it can be and is operated continuously for months at a time. Its efficiency and value is obvious.

The process of the Nutting patent, from which the Patent Office reasons that the process in suit should have been foreseen, starts with vinyl chloride. This, like ethylene, contains two carbon atoms connected by a double bond, and attached to one of the carbons are two hydrogen atoms and to the other are one hydrogen and one chlorine atom. The graphic formula is as follows:



This graphic formula is precisely like ethylene excepting that one chlorine atom has been substituted for one hydrogen atom. Since in the process at bar and in the Nutting process the reaction occurs at the double bond, the Patent Office reasons that the substitution of the chlorine atom for one of the hydrogens should make no difference, and that any reaction involving only the double bond of the vinyl chloride ought to work just the same with the double bond of ethylene. If one were permitted in chemistry to hazard such predictions, this *prima facie* would look reasonable.

The chemical reaction set out in the Nutting patent is the same in kind as that before the court. That is, hydrochloric acid gas is added in the presence of a catalyst and the double bond is broken, the acid is disassociated and its two halves attach themselves to the two fresh bonds thus provided. Graphically the reaction is represented as follows:



Vinyl chloride. Hydrochloric Acid. Ethylidine chloride.

Obviously, this reaction is diagrammed in a manner precisely analogous to that of the reaction in suit. So far as one can judge from the superficial view afforded by the formulae, one might be justified in guessing that very likely the two reactions might be alike.

But the present case is one of the best possible demonstrations of the wisdom of the rigid rule that prediction from analogy is taboo in chemical patent cases. In the District Court plaintiff called Henry B. Hass, head of the Department of Chemistry at Purdue University, who has made a special study of the particular group of chemicals here involved and who was awarded the Modern Pioneer Award of the National Association of Manufacturers for his research on this particular branch of chemistry. We tried to bring before the court the best man in the United States on this subject, and we think we did.

Doctor Hass points out (Rec. 23) the superficial similarity which would impress a chemist not very familiar with the two starting materials. He says, however, that the chemical and physical properties of vinyl chloride and ethylene are widely dissimilar. Ethylene is more sluggish towards practically every reagent which attaches itself to the double bond, while vinyl chloride is exactly the opposite, extremely reactive.

He points out that the vinyl chloride tends to polymerize readily, one molecule attaching itself to another similar molecule to form larger ones, until finally huge molecules are formed which make the synthetic resins. He points out two commercial resins formed in this way principally from vinyl chloride.

Second, he says there is a wide difference between the boiling points of the end products of the reactions. Ethyl chloride, plaintiff's end product, boils at 12° C., while Nutting's boils at 58° C. Since in both cases, to operate continuously, the reaction zone must be held above the boiling point of the end product so that it may continuously distill off, Nutting's process must be run at a much higher temperature than plaintiff's. This is highly undesirable because the reaction with hydrochloric acid tends to reverse at temperatures as low as 58° C. for ethylidene chloride, free hydrochloric acid being liberated and vinyl chloride polymerized to a resinous "goo." So the net product of the Nutting process is the resultant of the desired reaction, and its direct opposite which destroys much of the desired material.

A third difference, which is of the greatest importance, is the nature of the polymers produced as an incident to the reaction. Ethylene, plaintiff's starting material, can be polymerized to a slight extent, but when this occurs the polymer is a fluid, like lubricating oil, which can easily be drained out of the reaction zone in the very small quantities in which it is produced. On the other hand, the polymerization of vinyl chloride produces a tarry, gummy, resinous material which will not drain out, but which plugs up the reactor and prevents genuinely continuous operations (Rec. 25).

From his actual highly specialized knowledge of the vinyl chloride, it was Doctor Hass' opinion in advance that the process would not operate in the satisfactory manner in which the process before the court operates.

Actual tests of the Nutting process were carried out by Mr. L. Amos. He first testifies that the plaintiff's semi-commercial plant, for running plaintiff's process before the court, was run to make 300 pounds a day of ethyl chloride, and that it ran continuously for months without any trouble due to clogging or stopping of the reaction. The operation was at atmospheric pressure at a temperature, a little above 12° C.

To compare with this, the Nutting process was run on a laboratory scale in glass apparatus which was produced before the court and offered in evidence. The apparatus was exactly the same that would be used in carrying out plaintiff's process on a laboratory scale. In running the Nutting process different solvents were used: one, the same solvent bath as was used in running plaintiff's process; and, second, Nutting's solvent, which was also his end product. Without going into a detailed analysis of the figures, it is enough to say that in the latter case the apparatus was run four hours, at the end of which time it was so plugged up with black tarry products formed by polymerizing vinyl chloride that the operation could not be continued longer. In the meantime only 30% of the vinyl chloride was transformed into the desired end product whereas 29½% of it turned into the black thick tar (Rec. 31). The actual reactor was offered in evidence.

In another typical run using plaintiff's preferred solvent, 42.7% of the vinyl chloride starting material was transformed into the desired end product and about 22.8% was turned into the black tar which clogged the apparatus after four and a half hours of operation.

During the trial, test apparatus was operated to show that, with the temperatures required, the Nutting starting material polymerized rapidly to form the dark, tarry by-product.

These actual operations demonstrate that Nutting's continuous variant of his process is an impractical, absurd suggestion. Nutting's major operations are conducted batchwise and give good commercial yields of 90% or more, whereas the continuous variant relied on to anticipate produces, as has just been shown, such low yields that it could not compete at all with the preferred batch operations.

The actual tests therefore demonstrate the widest possible difference between the reference process and that before the court, and while this difference might not have been expected by one not especially familiar with this narrow field of chemistry, the difference would have been expected by a genuine student thereof. Doctor Hass testified (Rec. 43) that, as a chemist familiar with these compounds, he would not be led to expect that a given operation practiced on vinyl chloride or ethylene could be practiced on the other. Instead of one process leading to the other it would lead directly away from it.

He testified clearly and explicitly that neither the Nutting disclosure alone, nor the Nutting and Curme together, lead to the plaintiff's process without the need for experiment, and that these patents would not lead to the conclusion that one could merely substitute ethylene for vinyl chloride and arrive at the process here involved.

Plaintiff's evidence is wholly uncontradicted and therefore demonstrates the widest possible factual differences between the processes of the art and the process in suit. The evidence fully demonstrates the wisdom of the courts in rejecting (in chemical cases) prediction based on superficial chemical similarities.

Defendant's only argument in the court below, and we assume the only possible one here, is that the Nutting process is technically operative because it can be run about four hours before it plugs up, and that, being technically operative, it is a satisfactory technical reference no matter how superior the process in suit may be.

This is an utterly unsound argument. We should not be interested in mere technical operativeness but in whether plaintiff has produced a functionally and commercially better process. The slightest changes have been held patentable where they increase output or yield. In *Webster Loom Company* v. *Higgins,* 105 U. S. 580, 592, it was held patentable to make changes which increased the output of the loom 25%. In the case of *Eibel Process Co.* v. *Minnesota & Ontario Paper Co.,* 261 U. S. 45, 55, the patent was sustained because a very minor structural alteration raised the speed of paper production from something under 500 to something over 600 feet a minute.

In the instant case, the process in suit produced vastly greater relative benefits. Not only is the transformation into the desired end product raised from between 30% and 60% up to more than 90%, thus showing an increase in speed of production of from 50% to 300%, but in addition the waste of nearly as much raw material is wholly eliminated. Besides, the process is rendered commercially continuous in the sense that it can be run for months, whereas the reference process would have to be stopped for cleaning every few hours. The process before the court is so vastly superior in every respect that patentability is conclusively established by these new functions.

Had the Patent Office been right in reasoning from prediction, it could not have anticipated that the process at bar would be materially better than the reference process. The discovery that it is enormously better in several different respects is clearly of that empirical nature which has always been considered patentable discovery in chemical cases.

In this connection attention may again be called to the case of *Toledo Rex Spray Co.* v. *California Spray Chemical Co.,* 268 Fed. 201 (C. C. A. 6th), where the court laid some stress on the fact that when our arsenic acid was substituted as a precipitant for the sulphuric acid of the prior art, an element of chemical control was introduced which was not present in the process of the art. In the same way here, the substitution of ethylene for vinyl chloride produces a vast increase in useful output and a corresponding decrease in material turned into useless tar, and also an enormous increase in the feasible length of commercial runs. These new functions render the substitution patentable, however obvious it may at first appear.

Conclusion.

On either of the grounds submitted, the decree below should be reversed. The Patent Office ought to follow the settled and generally accepted rules of chemical patent law and abandon prediction from superficial analogies as a ground for rejection.

In the case at bar it has been abundantly proven by uncontradicted evidence that, in the particular field here dealt with, prediction is in fact unreliable and leads to entirely false conclusions, and that plaintiff has made a tremendous practical advance in the industry, amply sufficient, under the ruling cases, to support a patent on any change however slight it may seem on superficial examination.

It is not deemed important to consider the claims in detail, since they are not attacked except on the broad ground of being non-inventive in the operation which they define. If the process is inventive, the claims should be allowed.

Russell Wiles,
George A. Chritton,
Charles J. Merriam,
Nelson J. Jewett,
Counsel for Appellant.

Chritton, Wiles, Davies & Hirschl,
2800 Board of Trade Bldg., Chicago,
Attorneys for Appellant.

March 27, 1941.

UNITED STATES
COURT OF APPEALS FOR THE
DISTRICT OF COLUMBIA

FILED APR 22 1941

Joseph W. Stewart

CLERK

BRIEF FOR APPELLEE

United States Court of Appeals for the District of Columbia

APPEAL No. 7791

THE DOW CHEMICAL COMPANY, APPELLANT

v.

CONWAY P. COE, COMMISSIONER OF PATENTS, APPELLEE

APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF COLUMBIA

BRIEF FOR THE COMMISSIONER OF PATENTS

W. W. COCHRAN,
Solicitor, United States Patent Office,
Attorney for Appellee.

JOSEPH L. KELLY,
Of Counsel.

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In the United States Court of Appeals for the District of Columbia

No. 7791

The Dow Chemical Company, appellant
v.
Conway P. Coe, Commissioner of Patents, appellee

APPEAL FROM THE DISTRICT COURT OF THE UNITED STATES FOR THE DISTRICT OF COLUMBIA

BRIEF FOR THE COMMISSIONER OF PATENTS

INTRODUCTION

This is an appeal from the judgment of the District Court of the United States for the District of Columbia (R. 49) dismissing appellant's complaint brought under Section 4915 R. S. (U. S. C., title 35, sec. 63) to authorize the Commissioner of Patents to issue to appellant a patent containing claims 22 to 34, inclusive, of the application of Edgar C. Britton, et al., Serial No. 44,252, for "Production of Alkyl Halides," filed in the Patent Office on October 9, 1935. Appellant is the assignee of this application.

THE BRITTON, ET AL. APPLICATION

The application of Britton, et al. relates to the preparation of alkyl halides, and more particularly to the preparation of alkyl chlorides.

The application specifically discloses (R. 63) the preparation of ethyl chloride. A reaction bath consisting of anhydrous tetrachloral-ethylene and anhydrous aluminum chloride is maintained at 25° C. Ethylene gas and hydrochloric acid gas, in substantially their combining proportions, are passed into the reaction bath. Ethyl chloride is produced and passes off from the reaction bath as a vapor, which vapor is subsequently condensed and collected. The process is continuous and is carried out at atmospheric pressure.

PRIOR ART PATENTS RELIED UPON BY APPELLEE

The prior art patents relied upon by appellee against the claims on appeal are as follows:

Curme, 1,518,182 (R. 123).
Nutting, et al., 2,007,144 (R. 124).

Curme Patent, No. 1,518,182 (R. 123)

This patent discloses a process of making ethyl chloride by reacting ethylene and hydrochloric acid in the presence of aluminum chloride as a catalyst. The catalyst is suspended in a suitable solvent. The process disclosed by this patent is a batch process which may be carried out with or without pressure, depending upon whether or not a catalyst is used, and at room temperature.

Nutting et al. Patent, No. 2,007,144 (R. 124–126)

This patent discloses a process of making ethylidene chloride by passing a gaseous mixture of vinyl chloride and hydrogen chloride into a reaction bath. This bath consists of a catalyst (aluminum chloride) suspended in an organic liquid such as trichloroethane or acetylene tetrachloride. The bath is maintained at a temperature above 12° C. (On p. 2, col. 1, lines 48–49 it is stated that the preferred temperature is between 15° and 60° C.) The bath is maintained below its own boiling temperature and under approximately atmospheric pressure (p. 1, col. 2, lines 19–20). The process may be carried out continuously (p. 2, col. 1, lines 14–15, and claim 6, line 8).

SUMMARY OF ARGUMENT

1. To use the continuous process and the particular solvent disclosed by Nutting to carry out the Curme process would not amount to invention. Therefore, the claims on appeal do not define invention over Curme in view of Nutting.

2. To substitute ethylene from the Curme process for vinyl chloride in the Nutting process would not amount to invention. Therefore, the claims on appeal do not define invention over Nutting in view of Curme.

3. Processes disclosed by Curme and by Nutting et al. are similar.

ARGUMENT

Appellant's Claim 22

Claim 22, which appellant has selected as representative of the appealed claims (R. 101), reads as follows:

> In a process for the production of ethyl chloride, the step which consists in passing ethylene and hydrogen chloride, under substantially anhydrous conditions, into a liquid reaction bath consisting substantially of aluminum chloride and a chlorinated lower aliphatic hydrocarbon having a boiling point above that of ethyl chloride, while the bath is maintained at a temperature above 12° C. and below the boiling temperature thereof and under approximately atmospheric pressure.

Curme in view of Nutting

Appellee takes the position that claim 22 does not define invention over the patent to Curme (R. 123) in view of the patent to Nutting et al. (R. 124–126).

The Curme patent discloses a process for the production of ethyl chloride by reacting ethylene with hydrogen chloride; that is, the Curme patent discloses a process for the production of the same substance to which appellant's claims are directed.

This Curme patent teaches:

The use of the same reaction substances as do appellant's claims (ethylene and hydrogen chloride);

The use of the same catalyst (aluminum chloride);

The use of a bath, or solvent for the suspension of the catalyst (p. 1, lines 73–76 of Curme);

The carrying out of the process at room temperature (which is above 12° C.);

The carrying out of the process at atmospheric pressure (p. 1, line 52 of Curme).

The Curme patent does not disclose a continuous process nor the use of the particular solvent. However, the selected claim 22 is not limited to a continuous process, and the solvent recited therein is commonly used in such a process. Furthermore, the Nutting, et al. patent discloses a continuous process that is quite similar to appellant's process and wherein the same solvent is used. Therefore, to carry out the Curme process continuously and to use a solvent as disclosed by the Nutting, et al. patent, would be an obvious expedient to a person skilled in the art.

Speaking of "skill," this Court in the case of *Minnesota Mining and Manufacturing Co.* v. *Coe,* 99 F. (2d) 986; 69 App. D. C. 217, 220, said:

> The word "skill" as used in the cases is equally applicable to a *chemist* as to a mechanic, and to a *laboratory* as to a work bench. [Italics added.]

Nutting et al. in view of Curme

Appellee further takes the position that the appealed claims do not define invention over the Nutting patent (R. 124–126) in view of the Curme patent (R. 123).

It is the position of appellee that the only real difference between the process as set forth in selected claim 22, for instance, and the process disclosed by the Nutting, et al. patent is that appellant's process is directed to the production of ethyl chloride, and the patent discloses a process for the production of ethylidene chloride. However, appellee asserts that the process disclosed by the Nutting, et al. patent could be used in the production of ethyl chloride, in view of the Curme patent, and such use would be the mere application of an old process to a different chemical. Such use would not amount to invention.

In *Kwik Set, Inc.* v. *Welch Grape Juice Co.*, 86 F. (2d) 945, 947, the Circuit Court of Appeals for the Second Circuit said:

> It is well settled that the application of an old process to a similar or analogous subject without change in the method of application or in the result obtained will not sustain a patent. *St. Germain* v. *Brunswick,* 135 U. S. 227, 10 S. Ct. 822, 34 L. Ed. 122. Pectin and gelatin lump because they are both gums and their lumping is avoided by exactly the same expedient. It is not necessary that two materials be exactly the same to be regarded analogous in the eyes of the law. *Powers-Kennedy Contracting Co.* v. *Concrete Mixing & Conveying Co.*, 282 U. S. 175, 51 S. Ct. 95, 75 L. Ed. 278; *Electric Boot & Shoe Co.* v. *Little* (C. C. A.) 138 F. 732.

In *Standard Brands, Inc.* v. *National Grain Yeast Corp.*, 308 U. S. 34, 37, it is said:

> The Circuit Court of Appeals below declared—"We think that it cannot be denied that the use of antacid or basic materials as neutralizers for acidity in respect to yeast is old in the art * * *. We think that Hayduck has simply set forth a technique which is useful in the manufacture of yeast under modern methods. Hayduck's disclosures do not attain to the dignity of invention. His process is the result of the exercise of the skill of the calling, the application of an old principle to a similar or analogous subject with no change in the manner of application and without any substantially different result." * * * we think this much be accepted as the better view.

The United States Supreme Court held in *Paramount Publix Corp.* v. *American Tri-Ergon Corp.*, 294 U. S. 464, 473:

> To claim the merit of invention the patentend process must itself possess novelty. The application of an old process to a new and closely analogous subject matter, plainly indicated by the prior art as an appropriate subject of the process, is not invention. *Brown*

v. *Piper,* 91 U. S. 37, 41, 10 O. G. 417; see *Pennsylvania Railroad Co.* v. *Locomotive Truck Co.,* 100 U. S. 490, 494, 27 O. G. 207; *Dreyfus* v. *Searle,* 124 U. S. 60, 64, 42, O. G. 491; *Concrete Appliance Co.* v. *Gomery,* 269 U. S. 177, 184, 185, 342 O. G. 507.

Similarity of processes disclosed by Curme and Nutting et al. patents

The two processes disclosed by the Curme patent and the Nutting, et al. patent are very closely related. Each of these patents discloses the addition of hydrogen chloride to a compound containing an olefinic double bond. Curme discloses adding hydrogen chloride to ethylene, and the Nutting, et al. patent discloses adding hydrogen chloride to vinyl chloride. These compounds are so closely related that a chemist would realize that a process for adding hydrogen chloride to vinyl chloride could be used for adding hydrogen chloride to ethylene. It is apparent that both compounds have a reactive olefinic bond. The fact that vinyl chloride, as compared with ethylene, has one hydrogen atom substituted by a chlorine atom would be understood as not interfering with or affecting the addition reaction.

It was decided in *L. Sonneborn Sons, Inc.,* v. *Coe,* 70 App. D. C. 97; 104 Fed. 230, that the mere substitution of one chemical for another in a chemical process is not invention. In that case this Court said:

> The substitution of triethanolamine for other organic stabilizers in the claimed invention was an "obvious adaptation" of materials plainly foreshadowed by the teachings of the prior art, and required for its accomplishment *"only search or research."* [Italics added.]

GENERAL REMARKS

Appellant contends that the continuous process disclosed by the Nutting, et al. patent is inoperative, and if it does operate at all, that the yield is small. However, appellant's witness, with reference to the yield of the Nutting continuous process, stated (R. 39):

> The yield in Run 7 was 53½% * * * Run 8 the yield was 65.2%.

This statement, it is submitted, is evidence that the Nutting patent discloses an operative continuous process.

The United States Supreme Court in *Telephone Cases,* 126 U. S. 536, speaking of operative process disclosures, said:

> * * * Some witnesses testified that they were unable to do it. This shows that they, with the particular apparatus they had and the skill they employed in its use were not successful; not that others with other apparatus perhaps more carefully constructed or more skillfully applied, would necessarily fail. As was said in *Loom Co.* v. *Higgens,* 105 U. S. 580, 586, when the question is, whether a thing can be done or not, it is always easy to find persons ready to show how not to do it.

The question of yield was presented to this Court in the case of *In re Blackmore,* 33 App. D. C. 428. In deciding the question, this Court stated:

> * * * The process is the same whether the yield is great or small, and the process alone is the subject matter of appellant's claims.

In *Goodwin Film and Camera Co.* v. *Eastman Kodak Co.,* 207 F. 351, 360, the court stated:

> The patent law does not require that an inventor shall have succeeded in bringing his art to the highest degree of perfection, but it is enough if the skilled in the art understand the process described and the specification point out a practical way of performing it.

Appellant points out that because of the inoperativeness of the Nutting continuous process portions of that patent have been disclaimed. However, the fact that appellant, who is the owner of the Nutting, et al. patent, has disclaimed (R.

116) certain portions of the specification and claims of that patent which disclose and claim a continuous process for the production of ethylidene chloride, is irrelevant and immaterial insofar as the claims on appeal are concerned. The Nutting, et al. patent is a reference for what it discloses, irrespective of the disclaimer. Furthermore, the owner of one patent cannot, by disclaiming subject matter from that patent, pave the way for the issuance of another patent to him on the same subject matter. Such practice, if permitted, obviously would extend the monopoly beyond the statutory period.

Appellant contends, further, that there is no suggestion of combining the teaching of the Nutting et al. patent with that of the Curme patent to continuously produce ethyl chloride in the manner set forth in the appealed claims, and that the mere combining of the teachings of these two patents amounts to invention. However, this argument is deemed untenable.

In *In re Harris,* 37 App. D. C. 374, 378, this Court said:

> That the entire process of applicant is not anticipated in any single reference is unimportant. It is sufficient if his several steps be found in different patents. (*In re Monds Appeal,* 16 App. D. C. 351–354; *In re Droop,* 30 App. D. C. 334; *In re Faber,* 31 App. D. C. 531.)

In the case of *In re Weitzel and Michael,* 17 C. C. P. A. 1079; 39 F. (2d) 669, claims to a chemical process had been rejected on several references, mainly textbooks and other publications. The applicant objected to the combination of the references and to the deductions made by the Examiner as to how these references could be combined to anticipate the claims. The Court of Customs and Patent Appeals, in holding the claims unpatentable, quoted with approval several statements made by the Board of Appeals, pertinent parts of which are:

> In view of the disclosures we are of the opinion that there is every reason to believe that the statement in Halleman-Walker textbook applies to esters of

> formic acid as well as to other members of the fatty acid group.
>
> * * * we consider these disclosures sufficient to raise a presumption at least that the reactions disclosed would apply to formamid and to hydrocyanic acid as to the nitrile of formic acid and, where there is no real reason to suppose that the result would not be produced there is no invention in trying it and finding out that the process is successful.

CONCLUSION

In conclusion it is submitted that none of the claims on appeal is patentable in view of the prior art patents cited, and that therefore the judgment of the lower court should be affirmed.

W. W. COCHRAN,
Solicitor, U. S. Patent Office,
Attorney for Appellee.

JOSEPH L. KELLY,
Of Counsel.

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